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CATALYTIC VALORIZATION OF BIOMASS: DEHYDRATION, HYDROGENATION AND HYDRODEOXYGENATION

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ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science, University of Helsinki, for public examination in Auditorium A110, Department of Chemistry, A.I. Virtasen aukio 1, on June 1st 2018 at 12 o'clock noon.

Helsinki 2018

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ISBN 978-951-51-4195-8 (Paperback)

ISBN 978-951-51-4196-5 (PDF)

Unigrafia
Helsinki 2018

ABSTRACT

Abundant and inexpensive lignocellulosic biomass combined with the wide variety of terpenes, isolable from plants, have emerged as the strongest candidates to replace raw oil as a feedstock in the production of chemicals. Through catalytic modification, biomass feedstocks can be converted to various value-added products that can be utilized in a broad selection of applications.

The literature review presents catalytic dehydration, hydrogenation and hydrodeoxygenation (HDO) as defunctionalization methods to synthesize value-added chemicals from multifunctional biomass-based substrates. For example, the hydroxyl groups of monosaccharides, sugar alcohols, and terpenoids can be removed with Brønsted or Lewis acid-catalyzed dehydration, generating versatile platform chemicals for mainly biofuel and polymer applications. Hydrogenation as a valorization method is presented through noble metal-catalyzed hydrogenation of C=C and C=O bonds of diverse lignocellulose-based substrates, for example, the conversion of monosaccharides to sugar alcohols. HDO is an efficient defunctionalization method for simultaneous reduction of unsaturated bonds and lowering the oxygen content of the substrates. Depending on the employed catalyst system, the reaction produces selectively or fully defunctionalized biomass-based products. The main themes of the literature review relate to the subject of the author's articles published in peer-reviewed journals.

The results and discussion section will cover the most significant findings and discussions from the author's publications. The first part of the section describes new one-step HDO system for the conversion of enlarged furfural derivatives to biofuel compatible alkanes employing $\text{Eu}(\text{OTf})_3$ and Pd/C as deoxygenation and hydrogenation catalysts, respectively. The second part will cover the development and study of the new and recyclable Ru/C-based catalysts for the synthesis of isosorbide from lignin-containing cellulose. In the final part of the section, the findings of a robust and highly efficient transition metal triflate catalyzed dehydration of alcohols and terpenoids to olefins are reported. All the publications have significance in the field of biomass valorization and catalytic synthesis of sustainable chemicals.

PREFACE

The work was done at the Department of Chemistry University of Helsinki during the years 2014-2018. First, I would like to thank Professor Timo Repo for giving me the opportunity to reach for the title of Ph.D. His guidance and encouragement during my studies was also immensely valuable. In addition, I would like to thank Dr. Jari Kavakka for his insightful advice and good ideas during our co-operation with Stora Enso. Stora Enso is gratefully acknowledged for providing the funding for this project.

I want to thank my mum Paula and dad Kalle for teaching me the importance of education. Without their parenting and instructions since my first day at school, I would not have had the perseverance, self-confidence and determination to apply to university let alone educate myself to highest degree possible.

The examples set by my older sister Piia and brother Teemu has given me the bravery to set my goals high. I am grateful to have the best role models paving the way for me.

I could not have done this work alone. For this, I am in a debt of gratitude to the whole CatLab group and all of the people who helped me during the studies, who stood by me when I needed assistance, encouragement and laughter. Special thanks to Pauli Wrigstedt, Kalle Lagerblom, Dr. Sari Rautiainen, Dr. Arno Parviainen and Dr. Markus Lindqvist for their assistance, advice and support.

My biggest supporter during the Ph.D. work, by far, has been my fiancé Marianna, who I would like thank with all of my heart for having the patience and strength to support me in my time of need.

Helsinki, 28th of November
Juha Keskiväli



LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following publications:

- I** Keskipäli, J., Wrigstedt, P., Lagerblom, K., and Repo, T. (2017). One-step Pd/C and Eu(OTf)₃ catalyzed hydrodeoxygenation of branched C₁₁ and C₁₂ biomass-based furans to the corresponding alkanes. *Applied Catalysis A: General*, **534**, 40-45.
- II** Keskipäli, J., Rautiainen, S., Heikkilä, M., Myllymäki, T.T.T., Karjalainen, J-P., Lagerblom, K., Kemell, M., Vehkamäki, M., Meinander, K., and Repo T. (2017). Isosorbide synthesis from cellulose with efficient and recyclable ruthenium catalyst. *Green Chemistry*, **19**, 4563-4570.
- III** Keskipäli, J., Parviainen, A., Lagerblom, K., and Repo T. (2018). Transition metal triflate catalyzed conversion of alcohols, ethers and esters to olefins. *RSC Advances*, **8**, 15111-15118.

Other related articles:

- IV** Wrigstedt, P., Keskipäli, J., Leskelä, M., and Repo, T. (2015). The role of salts and Brønsted acids in Lewis acid-catalyzed aqueous-phase glucose dehydration to 5-hydroxymethylfurfural. *ChemCatChem*, **7**, 501-507.
- V** Wrigstedt, P., Keskipäli, J., and Repo, T. (2016). Microwave-enhanced aqueous biphasic dehydration of carbohydrates to 5-hydroxymethylfurfural. *RSC Advances*, **6**, 18973-18979.
- VI** Wrigstedt, P., Keskipäli, J., Perea-Buceta, J., and Repo, T. (2017). One-pot transformation of carbohydrates into valuable furan derivatives. *ChemCatChem*, **9**, 4244-4255.

In this thesis, the publications are referred to by their Roman numerals.

AUTHOR'S CONTRIBUTIONS

Publication I

The author was responsible for the design of experiments and conducted the majority of the experimental work and analyses. Based on the results, the author prepared the original manuscript, which was revised by co-authors Pauli Wrigstedt and Kalle Lagerblom, who also conducted some experimental work and analyses. The work was done under the supervision of Professor Timo Repo.

Publication II:

The author was responsible for the design of experiments and conducted the experimental work and analyses with the help of Jaakko-Pekka Karjalainen, Dr. Sari Rautiainen, Marko Vehkamäki and Kalle Lagerblom. The X-ray powder diffraction measurements were mainly conducted by Mikko Heikkilä. X-ray photoelectron spectroscopy was conducted by Kristoffer Meinander at the Department of Physics in University of Helsinki. Dr. Marianna Kemell and Teemu Myllymäki contributed by conducting scanning electron microscopy measurements; additionally, Mr. Myllymäki conducted the transmission electron microscopy measurements. The work done by Mr. Myllymäki took place at the Department of Applied Physics in Aalto University. Based on the obtained results the author prepared the original manuscript, which was revised by co-authors. The work was done under the supervision of Professor Timo Repo.

Publication III:

The author was responsible for the design of experiments and conducted the majority of the experimental work and analyses. Dr. Arno Parviainen and Kalle Lagerblom assisted with the experimental work and analyses. Based on the results, the author prepared the original manuscript, which was revised by the co-authors. The work was done under the supervision of Professor Timo Repo.

ABBREVIATIONS

2-MF	2-Methylfuran
AcOH	Acetic acid
BMIM	1-Butyl-3-methyl imidazolium
BP	Bagasse pulp
DMF	2,5-Dimethylfuran
DMSO	Dimethyl sulfoxide
DP	Dissolving pulp
EtOAc	Ethyl acetate
FA	Formic acid
FDCA	2,5-Furandicarboxylic acid
GC-FID	Gas chromatograph equipped with flame ionization detector
GC-MS	Gas chromatograph equipped with mass spectrometer detector
GVL	γ -Valerolactone
HAA	Hydroxyalkylation-alkylation
HDO	Hydrodeoxygenation
HMF	5-Hydroxymethylfurfural
HPLC-RID	High-performance liquid chromatograph equipped with refractive index detector
LA	Levulinic acid
LBAE	Lobry de Bruyn-Alberda van Ekenstein
MCC	Microcrystalline cellulose
MCM	Mesoporous silica
MIBK	Methyl isobutyl ketone
N.d.	Not detected
NMR	Nuclear magnetic resonance
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
XRD	X-ray powder diffraction
XPS	X-ray photoelectron spectroscopy

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1 INTRODUCTION

The constantly growing energy demand and material consumption have resulted in increasing anthropogenic CO₂ emissions through the growing use of oil reserves. As a result, the worry of the climate change has affected the political atmosphere and decision-making, directing research towards finding new sustainable feedstocks to replace crude oil.^[1] Abundant, renewable, and versatile biomass feedstocks, such as lignocellulose and terpenes readily available from wood and plants, have been recognized as the best alternative to petroleum in chemistry applications.

Biomass provides a plentiful source of modifiable natural polymers and other versatile organic compounds for use by biorefineries and the synthesis of renewable platform molecules and fuel components. Biorefineries are facilities that convert biomass to biofuels, energy, and other value-added chemicals, analogously to oil refineries in petrochemistry. The multifunctional and oxygen rich composition of the biomass feedstocks are vastly different from the relatively unfunctionalized petroleum resources. Thus, the defunctionalization of biomass, also known as valorization, is currently a hot research topic globally.

In order to obtain suitable products to replace the petroleum-based equivalents, the oxygen content and functionality needs to be lowered through valorization methods, including scission of C-O bond as well as reduction of C=C and C=O double bonds.^[2] The recalcitrant nature of cellulose and hemicelluloses makes their direct valorization difficult, and commonly the polysaccharides are hydrolyzed to their structural monosaccharides prior to their valorization. The obtained monosaccharides and the biomass-based terpenoids can then be catalytically defunctionalized to different value-added chemicals, such as furfural, 5-hydroxymethylfurfural (HMF), isosorbide, and olefins.^[3-5] These chemicals have received plenty of attention due to their wide applicability in biofuel, polymer, and medicinal applications.^[6-9] Moreover, the use of cellulose, hemicelluloses, and terpenes in the production of the second-generation biofuels and chemicals avoids the ethical dilemma of using edible resources, which was a criticism to the first generation bioproducts.

The past decade has seen the opening of the first industrial-scale second-generation biorefinery producing wood-based fuel,^[10] and paper and pulp companies have just started to look for new possibilities to produce biomass-based products. This indicates that the biomass revolution has taken its first steps to reduce the oil-dependency and to overcome the reign of petroleum-feedstocks. Despite the outstanding results and scientific breakthroughs achieved in the field of biomass valorization, the work is far from done. In order to reach the maximum potential of renewable resources, the catalytic processes need to be enhanced, the product yields increased, and new methods developed to utilize these alternative substrates.^[11]

2 SCOPE OF THE THESIS

The thesis covers the catalytic dehydration, hydrogenation, and HDO of various biomass-based products, such as monosaccharides and terpenes, to value-added chemicals. In the beginning of the literature review the structures of cellulose, hemicelluloses, and terpenes are introduced. Additionally, the conversion of hemicelluloses and cellulose to their structural monosaccharides will be briefly discussed. Next, the theory and general reaction mechanisms of dehydration, heterogeneous hydrogenation, and HDO are presented. These are followed by an in-depth discussion about the valorization of the biomass-based sugars, polysaccharides, and terpenes to furfurals, isosorbide, and olefins. The main emphasis is on the modification of hemicellulose- and cellulose-based monosaccharides and their derivatives. The aim of the literature review is to provide sufficient background for the reader to understand the present status of this section of biomass modification, and to point out the areas requiring further improvement.

Some exclusions and restrictions had to be made in the literature review, as the magnitude and scope of the literature in this field is immense. The exclusions and restrictions will be mentioned where appropriate, and some references will be given for further reading. Comprehensive works on the excluded topics, such as modification of lignin,^[12] enzymatic hydrolysis,^[13] and homogeneous hydrogenation^[14] have been published earlier.

The aim of the experimental part of the thesis was to develop tools for efficient conversion of the biomass-based substrates to value-added chemicals. In this respect, a lot of work has been done on optimization of the reaction conditions and development of catalysts and catalyst studies in general. The results and discussion will cover the most significant findings in the author's publications **I-III**. The discussion will further highlight the relevance of the key findings in the field. Detailed description of the studies can be found in the published articles, which are attached at the end of the thesis. The first article (**I**) covers the conversion of biomass-furfurals to diesel-ranked alkanes *via* aldol condensation and HDO. The second study (**II**) examines the conversion of cellulose to isosorbide, and the development of a recyclable hydrogenation catalyst for this reaction. The third article (**III**) addresses the upgrading of alcohols and monoterpene alcohols to olefins using abundant transition metal catalysts.

3 LITERATURE REVIEW

3.1 HEMICELLULOSES AND CELLULOSE

Polysaccharides, cellulose and hemicelluloses, are two of the three main components of dry wood and plant material called lignocellulose. Accordingly, polysaccharides are very abundant and readily available globally, for example, from residues of pulp, forestry, and agricultural industries. The abundance, availability, and non-edible nature of these polysaccharides makes them attractive feedstocks for the synthesis of second generation biomass-based chemicals and fuels.^[11]

3.1.1 CHEMICAL STRUCTURES

Cellulose and hemicelluloses are composed of monosaccharides connected to each other with glycosidic bonds.^[15] Cellulose composes solely of anhydroglucose units, which form chains with hundreds and even thousands units. The anhydroglucose units are bound with β -(1 \rightarrow 4)-glycosidic bonds from the anomeric C1 carbon to the C4 carbon of the following anhydroglucose unit (Figure 1). In addition, the hydroxyl groups in cellulose form intra- and intermolecular hydrogen bonds, giving cellulose additional mechanical strength and its recalcitrant nature. The highly regular assembly and hydrogen bonding gives cellulose its partially crystalline structure. Due to the crystallinity, the hydrolysis and the modification of cellulose is more challenging than that of the hemicelluloses.

The structures of hemicelluloses depends strongly on the source plant of the hemicelluloses, and it differs drastically to that of cellulose (Figure 1).^[16] Branched hemicellulose chains are composed of various sugars, pentoses (C₅ sugars), *e.g.*, xylose and arabinose, and hexoses (C₆ sugars), *e.g.*, mannose, glucose, and galactose, and different uronic acids. In contrast to cellulose, the monosaccharides in hemicelluloses are linked to each other in numerous different α - and β -glycosidic bonds, including β -(1 \rightarrow 4), α -(1 \rightarrow 2), and α -(1 \rightarrow 3) links.^[17] The naming of these bonds depends on the configuration, α or β , of the anomeric carbon (C1) and the carbon where the bond is formed in the following structural unit. In addition, the branched structure does not allow such an organized alignment of the hemicellulose chains compared to cellulose chains, and as a result, hemicelluloses are not as crystalline or recalcitrant as cellulose. The most significant hemicellulose classes are xylans and glucomannans, of which xylans are the most abundant hemicellulose in hardwoods and plants, thus xylose is the most abundant monosaccharide unit.^[17]

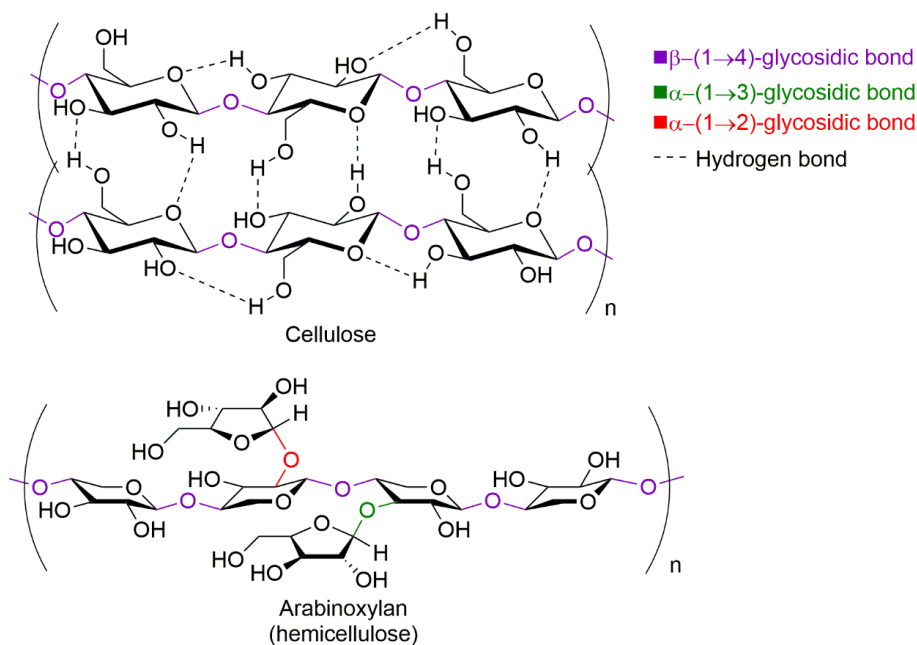


Figure 1 Example structures and glycosidic bonds of cellulose and xylan.

At the moment, cellulose and hemicelluloses are heavily used in paper and pulp applications. In addition to this, cellulose has various different industrial applications in different fields. For example, microcrystalline cellulose (MCC) is used as filler material in medicine tablets, and through chemical modification of cellulose various films (cellophane), emulsifiers, and thickeners (methyl- and carboxymethyl cellulose) can be produced.^[18,19] Likewise, hemicelluloses have applications outside the pulp industry and they have different functions in food and cosmetic industries. The potential of cellulose and hemicellulose in upgrading of biomass has been realized and they are predicted to play a central role in future production of biomass-based value-added chemicals.

3.1.2 SACCHARIFICATION

The first step in the conversion of lignocellulosic polysaccharides to smaller molecular weight value-added chemicals is the cleavage of the glycosidic bonds linking the long polysaccharide chains. Saccharification is a hydrolytic process, where the complex polysaccharide structures of cellulose and hemicelluloses are first broken into shorter poly- and oligosaccharides and finally into their fundamental monosaccharides and other fermentable sugars. During saccharification, both the glycosidic bonds binding the monosaccharides to each other and the network of the hydrogen bonds are broken using Brønsted acids such as H_2SO_4 , H_3PO_4 , HCl or enzymatic addition of water (Figure 2).^[20–23] Despite comprehensive research on the enzymatic

saccharification of lignocelluloses, the efficiencies of these systems do not match that of Brønsted acid-catalyzed hydrolysis.^[8] Thus, these enzymatic processes will not be covered further in this work.

It has been reported^[23,24] that acid-catalyzed hydrolysis of polysaccharides can occur in an acyclic or cyclic manner, depending on the position of the protonated oxygen (Figure 2). In general, the hydrolysis of glycosidic bonds occurs through initial protonation of the ether oxygen (Step 1). The protonation of the ether oxygen in the glycosidic bond results in a cyclic catalytic pathway, which is considered the main hydrolysis mechanism of the polysaccharides, and the protonation of the cyclic ether oxygen in the monosaccharide ring triggers the acyclic pathway. The protonation is followed by cleavage of the C-O bond, resulting in the formation of a carbocation and an alcohol on opposite sides of the broken bond (Step 2). Next, a water molecule attacks the carbocation, and after deprotonation a hydroxyl group and new anomeric center are formed (Step 3).^[23,25] This sequence is continued until the polysaccharides have been reduced to oligo- and monosaccharides.

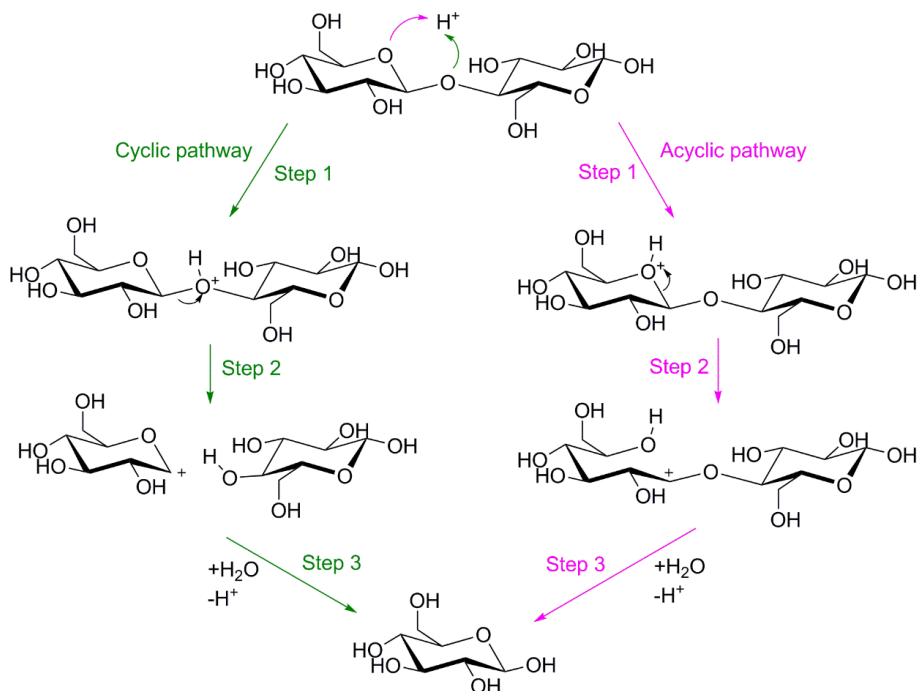


Figure 2 Proposed cyclic and acyclic mechanisms of the acid-catalyzed hydrolysis of glycosidic bond of cellobiose.^[23,24]

Due to their high efficiencies, many processes involving homogeneous acids, such as H_2SO_4 and HCl for catalytic hydrolysis and saccharification of cellulose and hemicelluloses have been developed.^[23] The use of the established laboratory-scale methods employing homogeneous acids ensures

inexpensive, fast, and complete conversion of the polysaccharides compared to enzymatic and heterogeneous methods. For example, up to 96% yield of xylose has been obtained from corn stover using 1 wt.% H_2SO_4 at 190 °C.^[26] Glucose has been reported to be obtained in high yield of 91% from cellulose using only 0.07 wt.% H_2SO_4 at an extreme temperature of 235 °C.^[27] Despite the high yields at the laboratory scale, no commercially feasible process of homogeneous acid-catalyzed saccharification has been developed.^[28]

In addition, from the industrial point-of-view the drawbacks of the homogeneous catalysts are numerous, including formation of waste, corrosion of the reaction vessels and troublesome and more complicated down-stream processes, for example energy intensive and cumbersome recycling of the catalyst.^[23,29] As a result, a lot of effort has been put into the development of new more effective and inexpensive heterogeneous catalysts. Indeed, various different heterogeneous acids, such as modified activated carbon, metal oxides, and ion exchange resins, have been reported to work in laboratory scale producing high conversions but producing only moderate monosaccharide yields.^[30–33]

Overall, the hydrolytic process of saccharification generates monosaccharides from cellulose and hemicelluloses, which are needed for the synthesis of small value-added chemicals. In this respect, saccharification can be considered as the first step in the valorization of biomass. The crystallinity and the more organized structure of cellulose makes the hydrolysis relatively difficult compared to amorphous hemicelluloses and, as a result, higher temperatures, stronger acid concentrations or longer reaction times are needed to achieve effective saccharification. The demanding saccharification conditions of cellulose and hemicelluloses usually results in follow-up reactions of the monosaccharides, such as formation of furfural, HMF, levulinic acid (LA), and formic acid (FA). Consequently, the reactivity of the monosaccharides has been utilized, as many methods have been developed to convert cellulose and hemicelluloses to the biomass-based chemicals in one-pot reactions.^[34–36] One-pot polysaccharide conversions to value-added chemicals will be covered in more detail in the appropriate chapters.

3.2 TERPENES AND TERPENOIDS

Alongside with cellulose and hemicelluloses, terpenes are a naturally occurring diverse class of strongly odored organic compounds which plants, such as coriander, balm trees, and citrus fruits, produce for various purposes.^[37,38] A myriad of roughly 30000 different terpenes have been recognized, thus they offer a versatile library of substrates for different applications.^[38] The building block of terpenes is isoprene unit (C_5H_8), occurring in various multiples, according to the isoprene rule. The terpene skeletons can form both acyclic and cyclic structures (Figure 3). In these structures, the isoprene building units are usually connected in a head-to-tail

manner (1-4 link), although there are some exceptions to this linkage, *e.g.*, in cyclic structures 3-4 links as well as other links may occur. By definition, the terpene backbone consists of at least one C=C double bond, but they can also have additional functionalities, such as alcohols, thiols, ketones, and aldehydes, these are then called terpenoids. In addition, aromatic benzene ring structures, such as cymenes, are possible. Depending on the number of the isoprene units, terpenes are divided into different classes according to their size, for example, hemiterpenes (one isoprene unit), monoterpenes (two isoprene units), and sesquiterpenes (three isoprene units). Lighter, volatile terpenes, mainly hemi- and monoterpenes, are isolable from plants *via* steam distillation as essential oils, while the heavier terpenes, sesquiterpenes and larger ones, are extracted from dried plant material.^[38,39] This work will mainly cover monoterpenes and their modification.

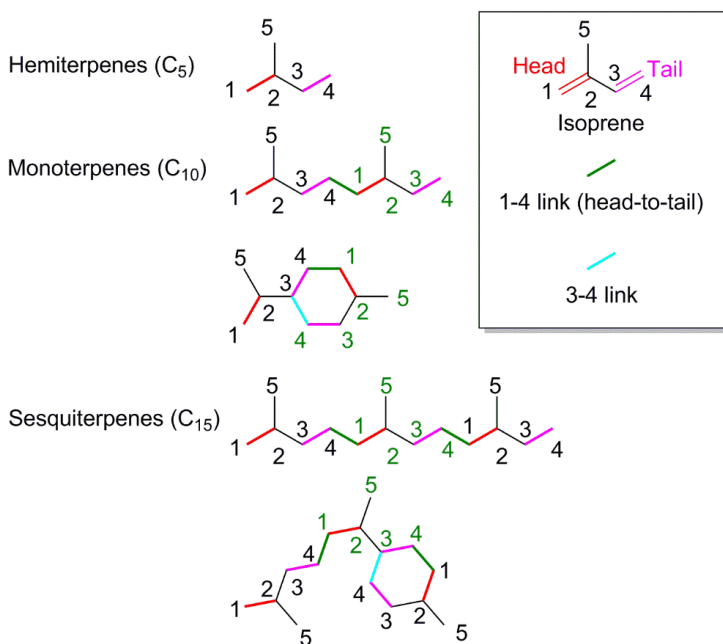


Figure 3 Examples of carbon backbone structures of terpenes and links. The functionalities have been left out for clarity.

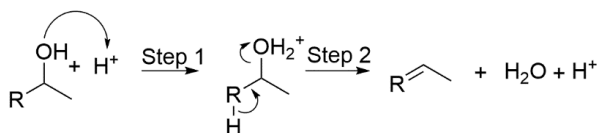
Currently, the diverse terpenes are used in food, cosmetic, and pharmaceutical applications, because of their strong taste, scent, and medicinal properties.^[40,41] Due to the abundance and versatility of terpenes, they can be utilized as a sustainable feedstock for the production of biomass-based value-added chemicals. Despite having the highest energy content of the biomass-based products, the use of terpenes as biofuels has been excluded, as they are produced in relatively low amounts.^[39] However, it has been estimated that 5-8% of the global production of petroleum is used in polymer and chemical applications while energy production and transportation fuels

consume around 90%.^[42,43] In this respect, the use of terpenes in smaller scale chemical and polymer applications could have an impact on reducing the use of fossil feedstocks. Overall, the unsaturated carbon chain in combination with the other functional groups of terpenes make them promising building blocks for the production of renewable fine chemicals, green plastics, and composites.^[39,44]

3.3 DEHYDRATION

Dehydration is a reaction where a water molecule is removed from the substrate molecule, typically an alcohol, forming an alkene or other unsaturated product depending on the substrate.^[45] Since the hydroxyl group (-OH) is a poor leaving group as such, the reaction is commonly catalyzed with Brønsted or Lewis acids. The use of a Brønsted acid catalyst facilitates the dehydration by initially protonating the hydroxyl group (Figure 4, Step 1). The protonated alcohol group ($R-H_2O^+$) is a better leaving group than the hydroxyl group and, as a result, it is eliminated as water. Simultaneously, a C=C double bond is formed in the carbon skeleton of the substrate, according to Zaitsev's rule, through release of the β -proton and concurrently closing the catalytic cycle (Step 2). The dehydration can be conducted with Lewis acid catalysts as well.^[46] This reaction proceeds through the bonding of the Lewis acid to the lone electron pair of the hydroxyl oxygen (Step 1). The electrophilic nature of the Lewis acid lowers the electron density in the alcohol C-O bond, resulting in cleavage of the alcohol C-O bond and the formation of alkene and Lewis acid hydroxide species (Step 2). The Lewis acid hydroxide reacts with the released β -proton, forming water and the original catalyst species (Step 3).

Brønsted acid catalyzed dehydration



Lewis acid catalyzed dehydration

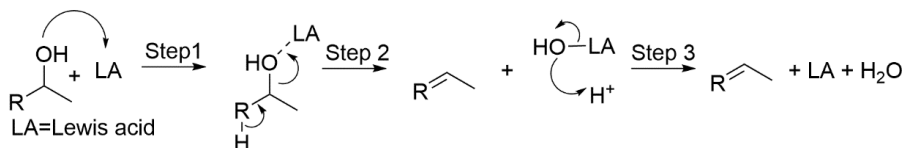


Figure 4 The dehydration mechanisms with Brønsted and Lewis acid catalysts.

Owing to the abundance of hydroxyl groups in a wide variety of natural substances, dehydration reactions are one of the most important ways to modify and valorize biomass. As a result, there are countless different

interesting dehydration products available from biomass (Figure 5). In the following chapters, the dehydration of monosaccharides, sugar alcohols, and monoterpene alcohols will be introduced. The emphasis of the recent studies has been on the dehydration of monosaccharides and sugar alcohols to furfurals (HMF and furfural) and isohexides (isosorbide), as a result, their synthesis and applications have been investigated extensively.^[39,47] Although the dehydration of monoterpene alcohols to olefins has been paid less attention than the dehydration of sugars and sugar alcohols, the terpenoid-based olefins are apt to be used as monomers in the synthesis of biopolymers.^[44]

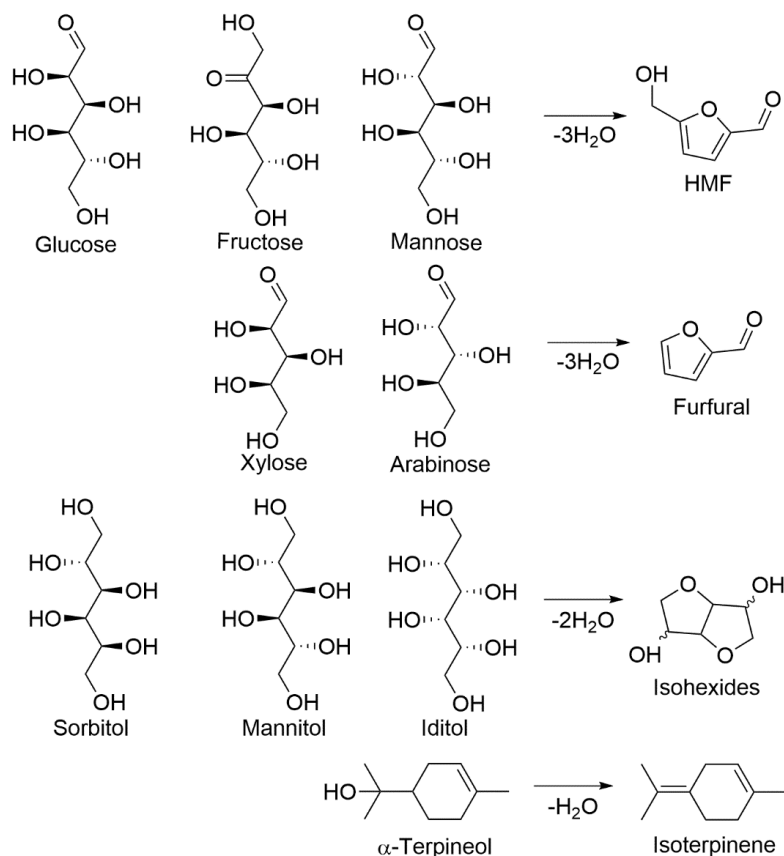


Figure 5 Examples of value-added chemicals obtained through dehydration of biomass-based sugars, sugar alcohols, and terpenoids.

3.4 HYDROGENATION

Hydrogenation is a reaction where hydrogen atoms are added to an unsaturated compound to reduce the double and triple bonds. Gaseous

molecular hydrogen (H_2) and other compounds (transfer hydrogenation) can be used as the hydrogen sources in this reaction. However, the addition of hydrogen does not take place without a catalyst, and therefore, the reaction is catalyzed with homo- or heterogeneous catalysts to facilitate the reaction in a laboratory or industrial environment within a feasible timescale. The literature review will mainly cover heterogeneous systems with solid noble metal hydrogenation catalysts and molecular hydrogen as the hydrogen source.

Under the present understanding, the heterogeneous hydrogenation with solid metal catalyst and H_2 as the hydrogen source follows the Horiuti-Polanyi mechanism.^[48] First, the hydrogen molecule is chemisorbed on the surface of the catalyst, followed by scission of the H-H bond producing two adsorbed hydrogen atoms (Figure 6, Step 1). After the scission of the H-H bond, the unsaturated substrate is adsorbed on the catalyst (Step 2). This is followed by the opening of the double bond through chemisorption (Step 3). The hydrogen atoms are transferred to the chemisorbed substrate on the surface of the catalyst in a stepwise manner, of which the first hydrogen transfer is reversible (Steps 4 and 5). The second hydrogen transfer then forms the reduced reaction product that, in a final step, is desorbed from the surface of the catalyst, thus completing the reaction cycle.

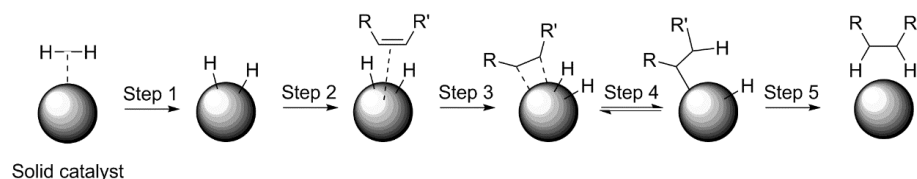


Figure 6 Example of heterogeneous hydrogenation according to the Horiuti-Polanyi mechanism.^[48]

Hydrogenation is and has been one of the most fundamental reactions in chemistry for the past century. The importance of this reaction is highlighted at the moment, as hydrogenation is commonly used method to valorize biomass-based compounds.^[49] Nature produces many different unsaturated products, including the C=C double bonds in the general terpene skeletons and the carbonyl groups in the structural aldoses and ketoses of cellulose and hemicelluloses. The hydrogenation of these biomass-derived monosaccharides produces sugar alcohols. For example, the hydrogenation of glucose and xylose, the main monosaccharides in lignocellulosic biomass, produces sorbitol and xylitol, respectively. These sugar alcohols are produced in vast amounts annually, due to their use in the food, pharmaceutical, and cosmetic industries.^[50,51] In addition to the traditional uses of sugar alcohols, they have been identified as valuable substrates in the synthesis of platform chemicals and intermediates for different potential industrial applications, thus helping in the replacement of fossil-based feedstocks.^[39,47] Also, dehydration products of monosaccharides, the furfural and its derivatives, can

be further upgraded through hydrogenation. These hydrogenation products can be used as solvents, biofuels, and monomers.^[52–54] The use of hydrogenation of biomass-based substrates will be covered in more detail in the appropriate chapters case-by-case.

3.5 HYDRODEOXYGENATION

HDO is a hydrogenolytic reaction where the substrate undergoes removal of an oxygen atom (deoxygenation) combined with simultaneous or subsequent addition of H₂ (hydrogenation). The removal of oxygen containing functionalities can occur through direct hydrogenolysis (C-O bond cleaved with H₂), dehydration (C-O bond cleaved through removal of water), decarbonylation (removal of CO), and decarboxylation (removal of CO₂).^[55] Accordingly, the HDO needs a suitable catalyst or catalysts to facilitate the formation of the desired reaction products. The catalysts usually contain noble metals as the hydrogenation catalyst as well as Brønsted or Lewis acidic sites to facilitate the cleavage of the C-O bonds.

The HDO mechanisms of different oxygen functionalities depend heavily on the reaction conditions and catalysts used. Taking into account the variety of different deoxygenation reactions and the oxygen containing functionalities the amount of their different possible combinations is so high that it is not reasonable to cover the mechanisms in detail here. Instead, the review article about HDO reported by He and Wang^[55] listed different HDO mechanisms for carboxylic acids, ketones, aldehydes, and alcohols (Figure 7). The relative HDO reactivities of oxygen-containing functionalities has been proposed to be alcohols>ketones>alkyl ethers>carboxylic acids.^[56] The relevant reaction mechanisms are explained in more detail in the appropriate chapters.

The aim of the HDO reaction is to reduce the high oxygen content of the biomass-based substrate and to reduce unsaturated bonds either selectively or completely.^[57] Typically, these HDO reactions require harsh reaction conditions in terms of temperature and pressure, which might result in formation of product mixtures through cleavage of C-C bonds and carbon skeleton rearrangement. In this respect, to achieve all-round defunctionalization and selective conversion of substrates, new catalytic systems need to be developed to remove the oxygen-containing functionalities efficiently under more benign reaction conditions. Recently, HDO systems have been studied intensively to harness their full potential in the modification of biomass to upgraded chemicals, such as liquid fuel alkanes, through complete defunctionalization of the substrates.^{[58–61],I}

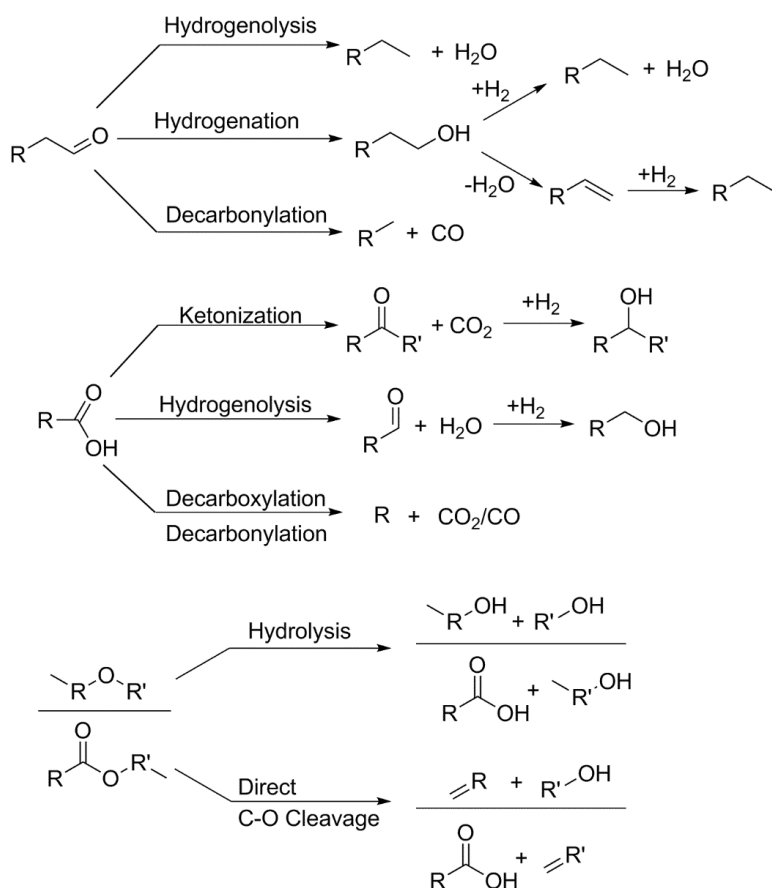


Figure 7 The HDO pathways depending on the oxygen moiety.

3.6 SYNTHESIS OF FURFURALS

3.6.1 GENERAL ASPECTS

Stepwise dehydration of C₅ and C₆ sugars form the multipurpose platform molecules, furfural and HMF, respectively. According to present understanding, the conversion of aldoses, glucose and xylose, is initialized by the isomerization to corresponding ketoses, fructose and xylulose, respectively. After this, the ketoses undergo three-fold dehydration to HMF and furfural. Furfural is synthesized from C₅ sugars, mainly from xylose, and different hemicellulose-containing feedstocks on an industrial scale.^[62] The most frequently used substrates for HMF synthesis are C₆ sugars glucose and fructose, although other substrates, such as mannose, cellobiose and starch have been reported as well.^{[7,63–65].IV,V} Thanks to the extensive research on these platform molecules, furfural and HMF can be modified in numerous ways to further upgraded chemicals to serve in a wide variety of applications

(Figure 8). The biomass-based furans can be used in the synthesis of biodiesel alkanes by growing the carbon chain, for example, *via* aldol condensation followed by complete defunctionalization with HDO.^[66–68] The selective hydrogenation and hydrogenolysis of the biomass-based furfurals produces 2-methylfuran (2-MF) and 2,5-dimethylfuran (DMF), highly wanted products in bioresin and fuel applications.^[6,57,69,70] Furthermore, through hydrogenation of the unsaturated furan ring, various tetrahydrofuran (THF) derivatives can be obtained.^[71,72] Diols, such as 1,5-pentanediol and 1,6-hexanediol can be synthesized from furfurals or their THF derivatives by a combination of hydrogenation and opening the heterocycle. These are highly valuable symmetric monomers for the synthesis of biopolymers.^[73,74] Though not covered in the thesis, HMF can also be oxidized to 2,5-furandicarboxylic acid (FDCA), which is expected to replace terephthalic acid in polymer and resin synthesis.^[75,76]

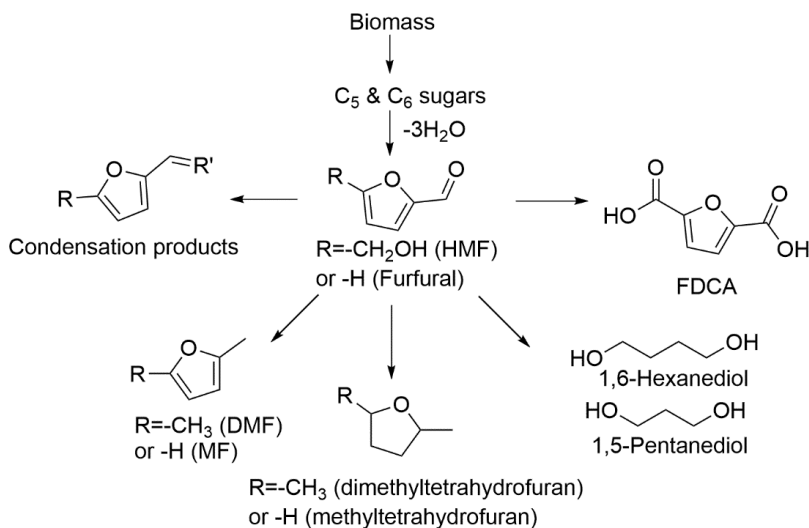


Figure 8 The conversion of furfural and HMF to further upgraded compounds.

3.6.2 ISOMERIZATION OF MONOSACCHARIDES

The isomerization between aldoses and ketoses can proceed through Brønsted acid- or base-catalyzed Lobry de Bruyn-Alberda van Ekenstein (LBAE) transformation or Lewis acid-catalyzed isomerization.^[77,78] For instance, the isomerization of glucose to fructose and xylose to xylulose can be enhanced with the use of metal catalysts, such as Cr-, Sn- or Al-based Lewis acids.^[78–84] The glucose-to-fructose isomerization reaction is initiated by the coordination of the Lewis acid catalyst to the aldehyde oxygen at the C1 position, followed by coordination and deprotonation of the hydroxyl group at the C2 position

(Figure 9, Step 1 and 2).^[78,83] Next, the catalyst is reported to facilitate the rate determining step of the intramolecular 1,2-hydride shift, resulting in the formation of a ketone to the C2 position (Steps 3 and 4). The Lewis acid catalyst is released when the oxygen at the C1 position is protonated to form fructose (Step 5). The isomerization of xylose to xylulose is thought to occur by the same mechanism.^[80,84] The LBAE mechanism proceeds through Brønsted acid- or base-catalyzed formation of 1,2-enediol, followed by rearrangement to the ketone.^[77] Because the LBAE transformation is considered primarily as base-catalyzed reaction, the significance of this transformation in the acid-catalyzed synthesis of furans from biomass-based sugars is negligible. Because of this, the reaction will not be covered in detail in this work.

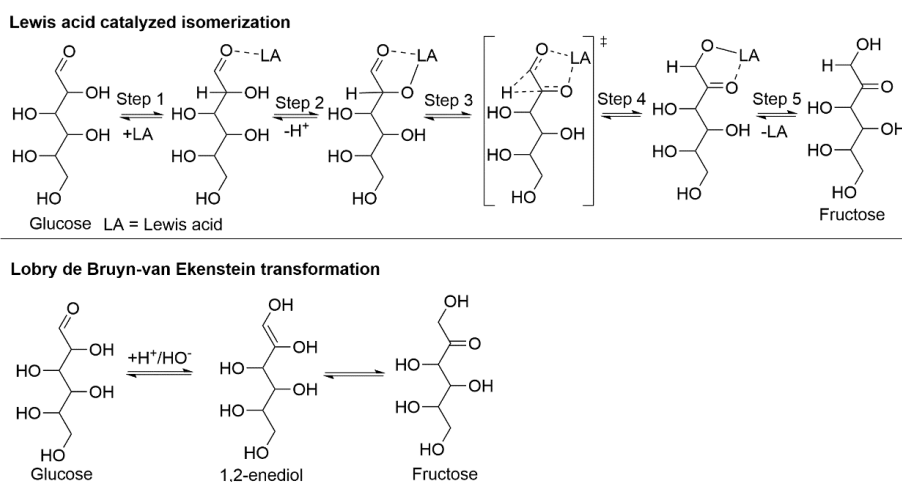


Figure 9 Lewis acid and Brønsted acid- or base-catalyzed isomerization mechanisms of glucose to fructose.^[77,78]

3.6.3 DEHYDRATION OF MONOSACCHARIDES

Different pathways have been proposed for the dehydration of C₅ and C₆ sugars to furfural and HMF, respectively (Figure 10).^[85–87] The enolization pathway, which is considered to be the most plausible one, is initiated by isomerization of aldoses to ketoses, as described earlier (Figure 10, Step 1).^[81,85] The first dehydration of fructose or xylulose forms an oxocarbenium ion, which then undergoes the rate-determining enolization through H⁺ abstraction (Steps 2–4). The enol then rearranges forming an aldehyde (Step 5), followed by two successive acid-catalyzed dehydrations, removing the hydroxyl groups from the five-membered ring structure (Steps 6 and 7). The alternative mechanism proposed for the formation of platform furfurals involves direct ring transformation of glucose and xylose.^[88,89] Xylose and glucose form mainly

six-membered rings, pyranoses. In solutions, these structures are converted to five-membered rings, furanoses, through acid-catalyzed dehydration of the hydroxyl group at the C2 position (Steps 1-3).^[88,89] The formed five-membered ring is then dehydrated twice to form HMF and furfural (Steps 4 and 5). The latter mechanism seems less efficient, as experimental studies have shown that, in the absence of a suitable isomerization catalyst, poor HMF yields from glucose are obtained.^[81,88] The reactivity difference between glucose and fructose toward dehydration is explained with the fact that glucose predominantly forms the more stable pyranose structure, whereas fructose forms the furanose structure, which is more susceptible to undergo protonation from the tertiary hydroxyl group.^[88] This protonation enables faster enolization and more facile formation of HMF.^[88]

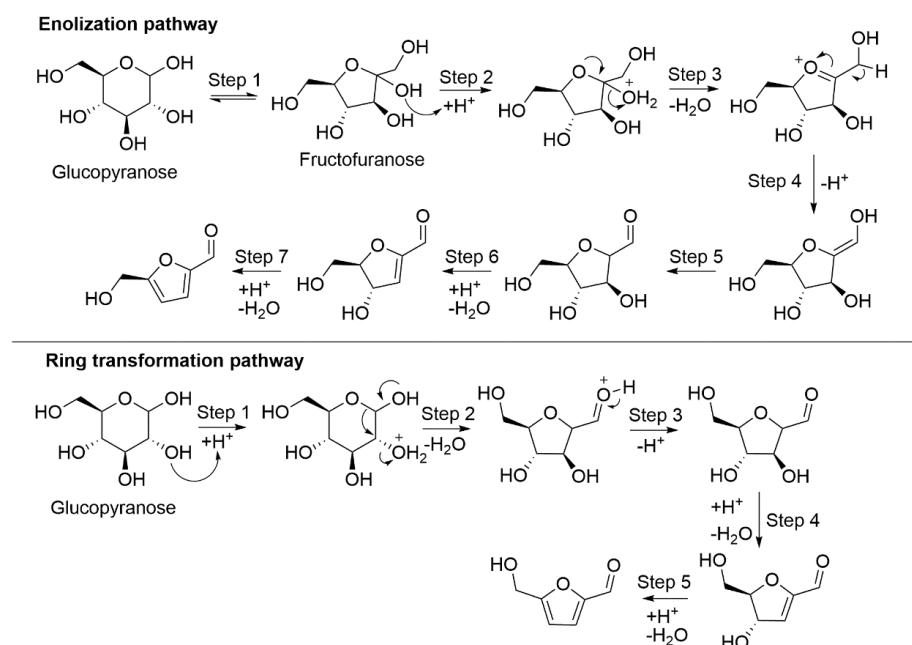


Figure 10 Presentation of the two proposed mechanisms for the dehydration of C₅ and C₆ sugars, using glucose as an example.^[81,85,88,89]

Although furfural and HMF are synthesized from similar substrates by identical reaction mechanisms, they are produced on different scales. The first large scale furfural synthesis process was developed by Quaker Oats in 1921.^[90] This original process has since been modernized to enhance the overall productivity and efficiency. The development of the system from batch type to continuous reaction has increased the efficiency and yield of the production process. Today, around 200000 tons furfural is produced annually mainly from agricultural lignocellulosic feedstocks, and furfural is largely used in the synthesis of furfuryl alcohol and THF compounds.^[6,72] At the moment, the furfural processes rely heavily on the use of homogeneous mineral acids, but

lately more ecological and sustainable heterogeneous acid catalysts have been studied, such as ion exchange resins, zeolites, and mordenites.^[29] However, with the most promising heterogeneous acid catalysts the furfural yields even from xylose are relatively low.^[29] To achieve commercial production of furfural using heterogeneous acids more advanced catalysts and reaction setups to convert xylan and hemicellulosic substrates to furfural are needed.

In contrast to furfural synthesis, the commercial implementation of HMF synthesis has not been feasible, due to the high price of the best substrate (fructose), complicated synthesis, and insufficient product yields from other monosaccharide or cellulosic substrates and laborious purification.^[91] Furthermore, the commonly used reaction conditions predispose HMF to side reactions, such as formation of insoluble humins through uncontrollable condensation, and hydrolysis to LA and FA in equimolar amounts.^[92] Although LA can be further converted to biomass-based solvent γ -valerolactone (GVL) through hydrogenation and dehydration (Figure 11),^[93] the relatively low demand for GVL and LA does not make the HMF synthesis economical.

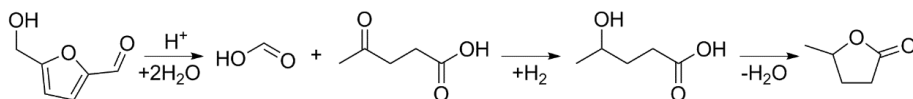


Figure 11 The rehydration of HMF to FA and LA and the conversion of LA to GVL.^[93]

The problems in the synthesis of furfurals, mainly HMF, has resulted in the development of myriad unique reaction systems and conditions in the search of the optimal reaction environment.^[4,7,94,95] These developed systems include the use of different homo- and heterogeneous Brønsted and Lewis acids to catalyze the dehydration. Also, different isomerization catalysts, *e.g.*, $CrCl_3 \cdot 6H_2O$, boric acid, and $AlCl_3$, have been reported to hasten conversion from glucose to fructose as well as from xylose to xylulose.^[83,96,97] Of these catalysts, Cr- and Al-based catalysts have been found to be most efficient and they are the most commonly used isomerization catalysts.^[7,98] It should be noted that the use of the isomerization catalysts is not beneficial when fructose or xylulose are used as substrates. In these cases, the ketose is converted to aldose according to the equilibrium, thus hampering the formation of the corresponding furfural. Alkali halide salts are often used as additives to enhance the furfural yields through improved product formation and separation.^[81,99] Furthermore, the reaction setups can be divided into mono- and biphasic as well as into conventional and microwave-induced heating. All these systems have their own versions of homo- and heterogeneous acids, isomerization catalyst, and additive combinations, resulting in countless recipes for the synthesis of furfurals.^[7,95] The recent studies have mainly focused on enhancing the synthesis of HMF, and overall

developing more sustainable reaction setups and routes for the synthesis of biomass-based furfurals.

The monophasic dehydration of monosaccharides offers a rather simple reaction setup for the synthesis of HMF and furfural. The system is based on a solvent or miscible solvent mixture of water, organic solvents or ionic liquids, capable of dissolving the substrates.^[79,100,101] For example, HMF has been reported to be generated in outstanding 100% yield from fructose using Amberlyst-15 as the catalyst and dimethyl sulfoxide (DMSO) as the solvent.^[101] The dehydration of glucose and fructose with *N*-heterocyclic carbene-chromium complexes in the ionic liquid [BMIM][Cl] produces 81% and 96% yields of HMF, respectively, thus highlighting the reactivity difference of the monosaccharides.^[102] A H₂SO₄-KBr-1,4-dioxane monophasic setup combined with microwave heating generates HMF in up to 81% and 78% yield from fructose and inulin, respectively.^{vi} Moreover, this approach allows further one-pot derivatization of HMF to various valuable products in good 77-94% yields. Furfural has been obtained from xylose and xylan also in very good yields of 82% and 85%, respectively, in a monophasic [BMIM][Cl] system with a highly recyclable AlCl₃ catalyst.^[103] Despite the high product yields, there are a few problems related to these monophasic solvent systems in the synthesis of furans. The used organic solvents, such as DMSO and ionic liquids, are not usually very volatile, thus making the isolation of the products cumbersome and energy intensive. Also, there has been some discussion about the toxicity of the ionic liquids.^[104] The use of acidic water as a sole solvent is troublesome due to the increased rehydration of HMF to LA and FA as well as the formation of humins resulting in decreased yields of HMF.^[105] As a result the reactions in monophasic aqueous solutions need to be conducted at relatively low temperatures, generating only modest yields of HMF compared to the other monophasic solvent systems.^[106,107]

The problems related to the monophasic reaction setups have inspired the development of biphasic setups. These setups combine an acidic aqueous phase and an immiscible organic phase, in which the aqueous phase acts as the reactive environment where the substrates and the catalysts form furfurals. The organic phase then extracts and stores the formed furfural, thus lessening the side reactions. The biphasic systems allows the use of more volatile organic solvents, thus easing the isolation of the crude HMF and furfural. Dias *et al.*^[108] have shown that furfural can be synthesized in similar yields of 76% in biphasic water/toluene mixture instead of plain DMSO solution with the heterogeneous sulfonic acid functionalized catalyst, coated MCM-41-SO₃H. Using a combination of water-DMSO/methyl isobutyl ketone(MIBK)-dichloromethane biphasic system up to 87% yields of HMF have been obtained from fructose using HCl as the dehydration catalyst.^[63] In addition to the use of biphasic systems, the use of alkali-halide salts as additives improves the formation of HMF, the separation of the phases, and extraction of the furfurals from aqueous phase to organic phase through the salting out effect, which increases the HMF yields through minimizing the side

reactions occurring in acidic water phase.^[81,99],^{IV,V} The better separation of phases with aqueous salt solutions allows the use of organic solvents that would otherwise be miscible with water, for example acetonitrile, GVL, and different alcohols.^[109],^V In addition to the enhanced phase separation, the halide anions are also known to catalyze the dehydration of fructose to HMF through enhanced enolization step in the sugar dehydration.^[81,98] The effectiveness order of the halides varies in aqueous and organic solutions, but Br⁻ has been reported to generate the highest yields of HMF in both solution types.^[110],^{IV,V} Using a saturated KBr aqueous solution and biomass-based GVL as a solvent in Amberlyst-38 and CrCl₃•6H₂O-catalyzed dehydration of glucose and fructose, very good HMF yields of 74% and 88%, respectively, has been obtained.^V Some studies of HMF synthesis with cellulose-based substrates have been published, reporting around 60% yields of HMF at best.^[35,95,111] Unfortunately, these laboratory-scale syntheses are not efficient enough to be implemented on larger scales and further development is needed.

3.6.4 SYNTHESIS OF 1,5-PENTANEDIOL AND 1,6-HEXANEDIOL

Due to the promising results from the laboratory-scale synthesis of HMF and the present large-scale production of furfural, the applicability of these compounds for various purposes has been studied extensively in recent years. The furfurals can be modified to suit various applications; herein some follow-up reactions of furfurals are presented within the scope of this thesis. The hydrogenation and HDO of furan compounds has been widely studied due to their capability of producing partially or completely defunctionalized products from biomass. For example, furfurals and their derivatives can be converted to different polyols, methylfurans, and alkanes, which are considered as important building blocks for biofuels and biomonomers of the future.^[52,60,112] The main emphasis of these studies has been on the biofuel and polymer applications, although utilizing the same reactions solvents and lubricants can be produced.

At the moment, suitable diols for polymer applications are produced mainly from petroleum.^[113] In this respect, the need for the synthesis of biomass-based diols is apparent. The hydrogenation and the following hydrogenolysis of HMF and furfural generates 1,6-hexanediol and 1,5-pentanediol, respectively. Usually, the catalysts contain a noble metal hydrogenation site (Pt, Pd, and Rh) and an acidic metal oxide site to facilitate the opening of the heterocycles.^[114] At first, the aldehyde functionality of the furfurals is hydrogenated, forming furfuryl alcohol compounds (Figure 12, Step 1). After this, the formation of 1,5-pentadiol and 1,6-hexanediol can proceed *via* two different mechanisms through furan or tetrahydrofuran ring opening. Xu *et al.*^[115] used a Li-modified Pt/Co₂AlO₄ dual-catalyst, and they showed that 1,5-pentanediol was formed through CoO_x-catalyzed furan ring opening followed by Pt-catalyzed hydrogenation of the C=C double bonds (Steps 2 and 3). Alternatively, when a Pd-Ir-ReO_x/SiO₂ catalyst was used, the

reaction was reported to proceed through Pd-catalyzed hydrogenation of the furfuryl alcohol to tetrahydrofurfuryl alcohol, followed by Ir-ReO_x-catalyzed THF ring opening through hydrogenolysis to 1,5-pentanediol (Steps 2 and 3).^[116] Moreover, up to 78% yield of 1,5-pentanediol has been achieved with an Rh-Ir-ReO_x catalytic system proceeding through THF ring opening.^[117] In contrast, a considerably lower 1,5-pentanediol yield of 35% was recorded with a Li-modified Pt/Co₂AlO₄ catalyst proceeding with the furan ring opening mechanism.^[115] The conversion of HMF to 1,6-hexanediol using Pd/ZrP has been reported to occur *via* the ZrP-catalyzed furan ring opening pathway, forming hexa-1,3,5-triene-1,6-diol, which is ultimately hydrogenated to 1,6-hexanediol with a Pd catalyst.^[118] In comparison, with a double layer Pd/SiO₂ + Ir-ReO_x/SiO₂, catalyst HMF is converted to 1,6-hexanediol *via* the THF ring opening pathway.^[119] In this setup, after the ring opening the intermediate, 1,2,6-hexanetriol, is dehydrated and hydrogenated to form 1,6-hexanediol as the product. Like the furfural conversions to 1,5-pentanediol, higher yields of 1,6-hexanediol are obtained from HMF with the THF ring opening pathway. The double layer Pd/SiO₂ + Ir-ReO_x/SiO₂ catalyst system generates 1,6-hexanediol in 58% yield from HMF, while the Pd/ZrP catalyst generated a 43% yield.^[118,119] Evidently, the choice of catalysts has a big effect on the reaction mechanism and the diol yields.

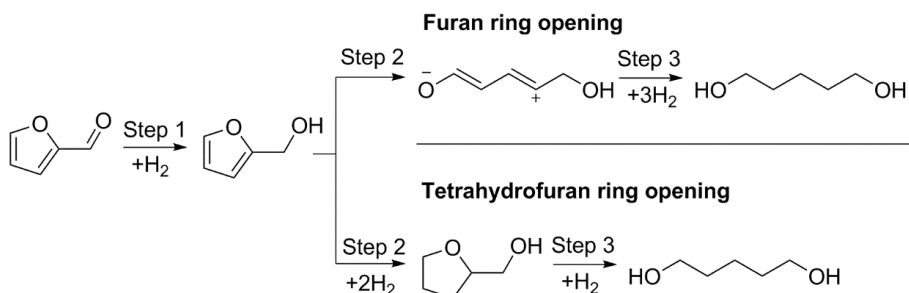


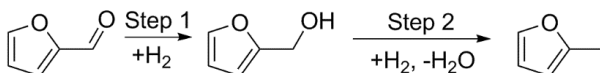
Figure 12 Proposed reaction pathways for the formation of 1,5-pentanediol from furfural.^[115–117]

3.6.5 SYNTHESIS OF DMF AND 2-MF

Furfural and HMF can be converted to highly desirable DMF and 2-MF biofuel components, respectively.^[59,60] The conversion of furfurals to DMF and 2-MF is conducted with selective hydrogenation and hydrogenolysis. The catalysts used facilitate selective hydrogenation of the carbonyl double bonds, leaving the unsaturated furan ring intact. Unlike the catalysts used in the diol synthesis, the catalysts used in the methyl furan synthesis do not contain an acidic site capable of opening the heterocycle under the reaction conditions used. The conversion of furfural to 2-MF goes through initial hydrogenation of the aldehyde to alcohol, followed by its hydrogenolysis to 2-MF (Figure 13, Steps 1 and 2).^[120] On the other hand, the synthesis of DMF from HMF can

proceed in two alternative ways; either, the hydroxyl group is first removed through hydrogenolysis, followed by the hydrogenation of the aldehyde functionality to alcohol and its subsequent removal, or *vice versa* (Figure 13).^[121]

Conversion of furfural to 2-MF



Conversion of HMF to DMF

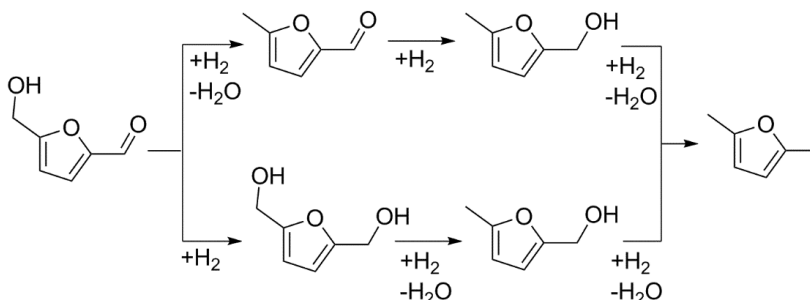


Figure 13 The formation of DMF and 2-MF from HMF and furfural.^[120,121]

The methylfurans can be synthesized with various different catalysts, Leshkov *et al.*^[122] published a momentous study on the hydrogenation and hydrogenolysis of HMF to DMF using copper chromite (CuCrO_4) and Cu:Ru/C (3:1 atomic ratio) as the catalysts, producing 61% and 71% DMF yields, respectively. Previously, copper chromite had been used to catalyze the conversion of furfural to 2-MF.^[123] In addition to the lower yield of DMF, the CuCrO_4 underwent rapid deactivation in the presence of chloride ions, whereas the combination of ruthenium and copper formed a catalyst that proved to be significantly more resilient towards chloride ions. Since then, several studies have been published reporting excellent (>90%) yields of DMF and 2-MF in just 2-5 hours using simple metal catalysts, such as Cu/SiO₂, Ru/C, and Pd/C.^[121,124,125] On the downside, the synthesis generally requires harsh reaction conditions in terms of temperature (up to 220 °C) and pressure (up to 20 bars) when molecular hydrogen is used as hydrogen source. Alternative hydrogen sources could facilitate the conversion of furfurals to methylfuran under more benign reaction conditions. For example, with the use of transfer hydrogenation of HMF to DMF with FA as the hydrogen source the reaction can be conducted at atmospheric pressure and lower (70 °C) temperature, the trade-off being the longer reaction time.^[126] This transfer hydrogenation system provides 51% yield of DMF from fructose in an overall reaction time of 17 hours.

3.6.6 SYNTHESIS OF BIOFUEL COMPATIBLE ALKANES

The synthesis of diesel-range alkanes from HMF and furfural is initialized by increasing the molecular weight, for example with aldol condensation or hydroxyalkylation-alkylation (HAA). These enlarged furan derivatives are then subjected to the HDO conditions, generating alkanes as products. During this reaction the substrates are defunctionalized through catalyst dependent opening of the heterocycle (THF or furan ring),^[112,127] decarbonylation,^[55] deacetylation^[128] or dehydration^[46,129],^I reactions in addition to hydrogenation of C=C and C=O double bonds.

The increase of the molecular weight using aldol condensation is generally conducted with a base catalyst, allowing the coupling of aldehyde (HMF or furfural) and ketone under mild reaction conditions. The properties of the furfural-derived alkane can be modified with the ketone selection. Acetone and MIBK are frequently studied as the condensation partners as they can be produced from biomass. When acetone is used in the aldol condensation with furfural or HMF, double condensation can occur, forming C₉ and C₁₅ or C₈ and C₁₃ products depending on the furfural used. In contrast, the benefit of using MIBK in the reaction is that it produces branched furan products, which form branched alkanes through HDO. These alkanes are highly desirable products for fuel applications, as they have lower freezing points and higher octane number than linear alkanes. The NaOH-catalyzed aldol condensation of furfurals has been conducted in a solvent-free and biphasic manner. The biphasic system requires a significantly higher amount of the base catalyst (at least 37 mol.% of NaOH) than the solvent-free system according to previous publications (13 mol.% of NaOH).^[130,131]^I The higher catalyst loading is partly due to HMF degradation in the presence of water and NaOH to acidic byproducts, LA and FA, consequently neutralizing the NaOH catalyst.^[131] Different heterogeneous catalysts, such as CaO, Mg-Al-oxide, and MgO-ZrO₂, have also been used to catalyze aldol condensation. Unfortunately, they require longer reaction times and higher temperatures to match the 96% yield of the condensate products obtained with monophasic NaOH-catalyzed aldol condensations.^[67,132,133]^{I,VI}

HAA is an acid-catalyzed reaction, which combines two 2-MF molecules with an aldehyde or a ketone, forming furylmethanes that can be converted to branched alkanes through HDO. The reaction proceeds through initial hydroxyalkylation, a coupling of aldehyde or ketone with 2-MF, which is followed by alkylation where the second 2-MF molecule is attached to the hydroxyalkylate (Figure 14).^[134] Various carbonyl compounds, including furfural, HMF, and MIBK, have been used in the HAA reaction catalyzed by suitable acids, such as Amberlyst resins, *para*-toluenesulfonic acid, and H₂SO₄, producing furylmethanes in high yields (up to 93%).^[61,134,135] Similarly to the aldol condensation, the HAA reaction conditions are rather benign.

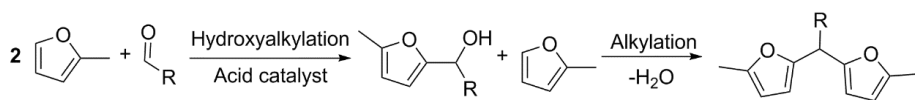


Figure 14 The formation of furylmethanes through HAA.^[134]

After increasing the molecular weight, the aldol condensation and HAA products are converted to alkanes with HDO. Generally, the HDO of the furfural derivatives reaction requires harsh conditions in terms of high temperatures and H₂ pressures. Because of these conditions, depending on the substrates and catalysts used a broad range of products can be formed, thus lowering the reaction selectivity. The HDO of furans is commonly conducted with a dual catalyst system in a single body or as separate catalysts, composing of hydrogenation catalyst and the C-O activating acidic catalyst. Although the HDO of furans can be conducted without the C-O activating catalyst, significantly higher temperatures are required for the hydrogenation catalyst alone. Yang *et al.*^[67] converted furfural and MIBK aldol condensate product to alkanes with use of only Pt/C, Ir/C, and Pd/C catalysts; as a result, the substrate conversion required a high temperature of 370 °C and 60 bars of H₂. Although high (>90%) alkane yields were obtained, the use of these catalysts and the forcing reaction conditions resulted in partial decarbonylation during the reaction, and as a result, the selectivity of reaction decreased. In this respect, the benefit of the C-O activating catalyst is highlighted by the report of a heterogeneous Ir-ReO_x/SiO₂ dual catalyst capable of producing a quantitative conversion and mixtures of C₈-C₁₅ alkanes in 82-99% yields from different furylmethanes at relatively mild temperature of 170 °C.^[58] The C-O activating part of the catalyst was ReO_x and hydrogenation was attributed to the iridium metal, SiO₂ being the support material. The Ir-ReO_x/SiO₂ catalyst was reusable after calcinating the catalyst at 500 °C for three hours. Furthermore, the mixture formation increased with increasing temperature, and it was guided by the stability of the formed carbocations. Similar formation of alkane mixtures has been reported with Pt, Ni, Ru, and Pd on SiO₂/Al₂O₃ supported catalysts at 230 °C under 60 bar of H₂ using different furylmethanes as substrates.^[61] Meanwhile, a highly selective Pd/NbOPO₄ catalyst is capable of producing a 94% yield of octane from furfural and acetone aldol condensation product in 24 hours at 170 °C under 20 bars of H₂.^[68] Also, this system has been stated to have an impressively long operation time of 256 hours in a fixed-bed reactor without catalyst deactivation in the synthesis of octane.

The use of metal triflates in combination with hydrogenation catalysts has been shown to efficiently catalyze the HDO of various furan compounds to corresponding alkanes in high yields.^[112,129] With the use of metal triflates the substrate undergoes little skeletal transformation during the removal of oxygen species, thus high selectivities are achieved. The conversion of furan compounds to alkanes has been commonly conducted in two reaction stages using neutral and acidic solvents.^[112,129] For example, using acetic acid (AcOH)

as solvent the conversion of HMF-based substrate to corresponding alkane has been reported to proceed through an initial acid-catalyzed furan ring opening to a triketone during heating at 100 °C for 3 hours (Figure 15, Step 1).^[112] The second stage of the reaction was conducted at 200 °C under 34.5 bars of H₂ for 16 hours, during which the ketones were hydrogenated to hydroxyl groups, which then underwent La(OTf)₃-catalyzed acetoxylation-deacetylation sequence (Steps 2-4).^[112,128] Consequently, C=C double bonds are formed, and through their subsequent hydrogenation with Pd/C and H₂ alkane is formed (Step 5).^[128] This two-step reaction pathway generates *n*-nonane from the HMF and acetone aldol condensation product in 90% yield and in a total reaction time of 19 hours.^[112] Alternatively, with neutral unreactive solvent, the two-staged reaction proceeds through complete hydrogenation of the furan compounds to corresponding THF-compounds at 60 °C under 50 bars of H₂ (Step 1).^[129] During the 20-hour second stage of the reaction the metal triflate opens up the cyclic structure and cleaves the oxygen moieties through dehydration, which is followed by the hydrogenation of the formed C=C double bonds with the effect of Pd/C at 180 °C under 50 bars of H₂, forming the corresponding alkane (Step 2).^[129] Using a combination of Hf(OTf)₄ and Pd/C as catalysts, *n*-nonane has been synthesized in a very good yield of 92% in a two-step reaction in a neutral solvent octane.^[129] This system also enabled catalyst recycling in five consecutive runs with only moderate 14% loss of *n*-nonane yield under the optimal reaction conditions. Moreover, 2-methylundecane and 2-methyldecane has been produced in high yields of 90% and 98%, respectively, in one-step manner with ethyl acetate (EtOAc) as the solvent using Eu(OTf)₃ and Pd/C as catalysts.[†] According to this study, the neutral solvent system seems to be more favorable for the conversion of furan compounds to alkanes. Additionally, due to the lack of primary hydroxyl groups, the conversion of furfural-based compounds to alkanes is more facile than the HMF derivatives.^{[68],†}

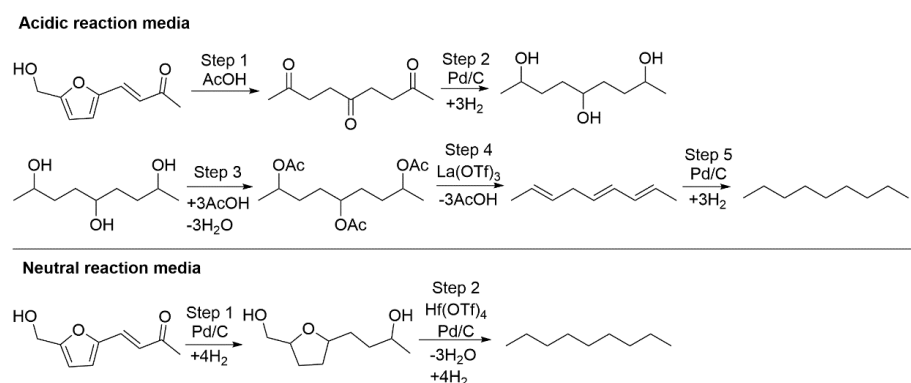


Figure 15 The M(OTf)_x- and Pd/C-catalyzed HDO reaction mechanisms in acidic and neutral solvents.^[112,128,129]

3.6.7 OVERVIEW OF FURFURALS AND THEIR APPLICATIONS

At the moment, these two versatile platform molecules, furfural and HMF, can be synthesized from monosaccharides, xylose, glucose, and fructose, as well as from polysaccharides, hemicelluloses and cellulose. Furfural is produced on an industrial-scale from various hemicellulosic materials, for example, agricultural and forestry residues, using mineral acid catalysts. The development of this synthesis mainly concentrates on replacing the mineral acids with solid acids to avoid the drawbacks of the mineral acid catalysts and ease the product purification and separation of the catalyst. Although some promising heterogeneous acid catalysts have been developed, the reaction setups and catalysts need further development to enable large-scale heterogeneous acid-catalyzed furfural production from polysaccharides. In comparison to furfural production, HMF synthesis is more difficult and cumbersome as HMF is prone to undergo oligomerization and hydrolysis side reactions. As a result, numerous different additive, catalyst and solvent system combinations have been developed for different substrates to ensure high yields. With the use of fructose as substrate, excellent yields are obtained; however, the use of glucose and cellulose as the substrates generate HMF in smaller quantities.

The combination of the recalcitrance of cellulose toward hydrolysis to glucose and its subsequent isomerization to fructose makes the HMF synthesis from cellulose challenging. AVA Biochem has a HMF production plant with a capacity to produce 20 tons of HMF per year; however, the substrate used is sugar cane-based sugar syrup.^[136] This underlines the lack of a large-scale HMF production from inedible feedstocks. Hence, more sophisticated methods should be developed to guarantee high yields of HMF from pure cellulose or even lignocellulose as substrates. This requires efficient catalysts for hydrolysis, isomerization, and dehydration combined with a high-performance reaction system, such as a continuous flow reactor merged with microwave heating.

The diverse furfurals can be converted to diols, DMF, MF, and diesel-ranged alkanes through hydrogenation and HDO. The further upgraded products can be utilized in different applications, such as biofuel and biopolymer synthesis. Through efficient synthesis of furfural and HMF from lignocellulose, various further upgraded products could be produced sustainably in larger amounts to reduce the use of their petroleum-based counterparts. However, the effective defunctionalization of the furfurals to these downstream products with the present methods requires generally long reaction times under forcing conditions, for example, high hydrogen pressures and high reaction temperatures. Consequently, side products are formed through skeletal transformation and over reduction, thus lowering the selectivity and resulting in wasted materials. Therefore, it is vital to develop more efficient catalysts and synthesis methods for these processes. In this sense, there is still plenty of room for development in the field of conversion

of C₅ and C₆ monosaccharides to biomass-based furans and their further upgrading to downstream products.

3.7 SYNTHESIS OF ANHYDRO SUGAR ALCOHOLS

3.7.1 GENERAL ASPECTS

In addition to the biomass-based furfurals, C₆ sugars, including glucose, mannose and idose, can be converted isohexides.^[47] The synthesis is initiated by the hydrogenation of the aldehyde group of glucose, mannose or idose generating the sugar alcohols sorbitol, mannitol, and iditol, respectively (Figure 16, Step 1). At the moment, these sugar alcohols are widely used as sweeteners and humectants.^[50,51] The sugar alcohols are then converted to the corresponding bicyclic isohexides (dianhydrohexitols) through two-fold acid-catalyzed dehydration (Step 2). In comparison to glucose and mannose, idose has little relevance in biomass modification since it is not a naturally occurring C₆ sugar. Similarly, C₅ monosaccharides can be converted to their corresponding anhydro sugar alcohols through hydrogenation and subsequent dehydration. For example, the hydrogenation of xylose produces xylitol, which can then be dehydrated to anhydroxylitol.^[137] Although the literature is filled with examples of hydrogenation of different monosaccharides to the corresponding sugar alcohols and their respective dehydration, the direct conversion of biomass-based polysaccharides to anhydro sugar alcohols, such as isosorbide and isomannide, is in high demand.^[3,138–141]

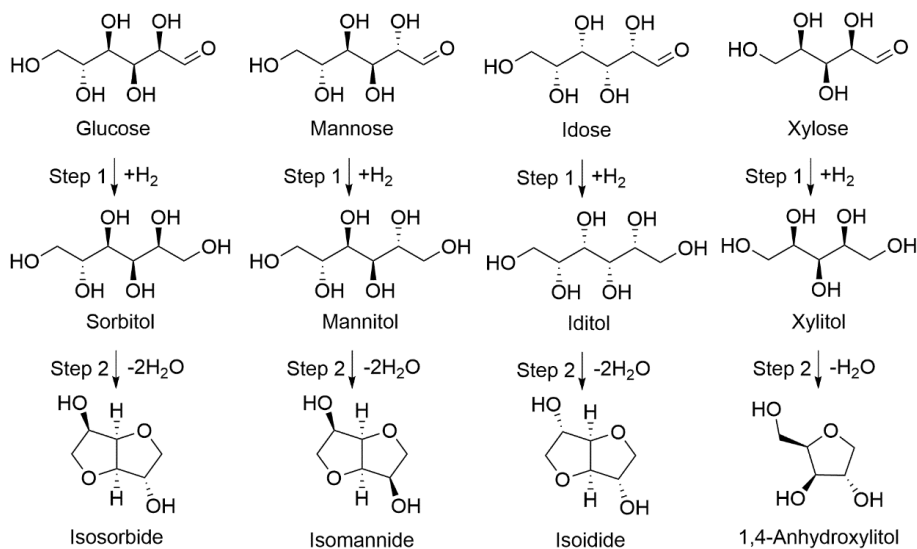


Figure 16 The conversion of C₅ and C₆ monosaccharides to anhydro sugar alcohols (isohexides and 1,4-anhydroxylitol).

The isohexides have been extensively investigated due to their high potential in polymer, medicinal, and fine chemical applications (Figure 17).^[8,47] In general, the polymer applications are viewed as the most promising field for the large-scale use of isohexides. For example, the use of isohexides as a comonomer in poly(ethylene terephthalate) have been shown to increase the glass transition temperature of the polymer.^[47,142] For further reading, comprehensive review articles has been published regarding the use of isohexides in polymer applications.^[8,47] In addition to their polymer applications, isohexides have various other potential uses. The new solvent ditetrahydrofuran can be produced from isomannide, through chlorination of the hydroxyl groups with thionyl chloride and subsequent reduction with Raney-Ni.^[143] In general, esterification, tosylation, and acetylation increases the reactivity of isohexides and, as a result, they can be converted to chiral auxiliaries and multidentate ligands.^[8] The nitration of isosorbide produces isosorbide dinitrate, which has been found to be effective in the treatment of *angina pectoris*. Moreover, a gel containing the carbohydrate derivatives, xylitol and anhydroxylitol, has been shown to promote the hydration level of skin, which is a useful quality in the cosmetic industry.^[144]

The stereoisomer isohexides mostly exhibit the similar properties in downstream applications, although some differences in the melting points and reactivities of the hydroxyl groups does appear. Due to the abundance of cellulose, and hence glucose, isosorbide is the most studied isohexide. This chapter will describe the present state of the production of anhydro sugar alcohols, emphasizing the conversion of cellulose to isosorbide. Although future applications of anhydro sugar alcohols are considered very important, further upgrading reactions fall outside the scope of this thesis, thus their detailed inspection has been omitted.

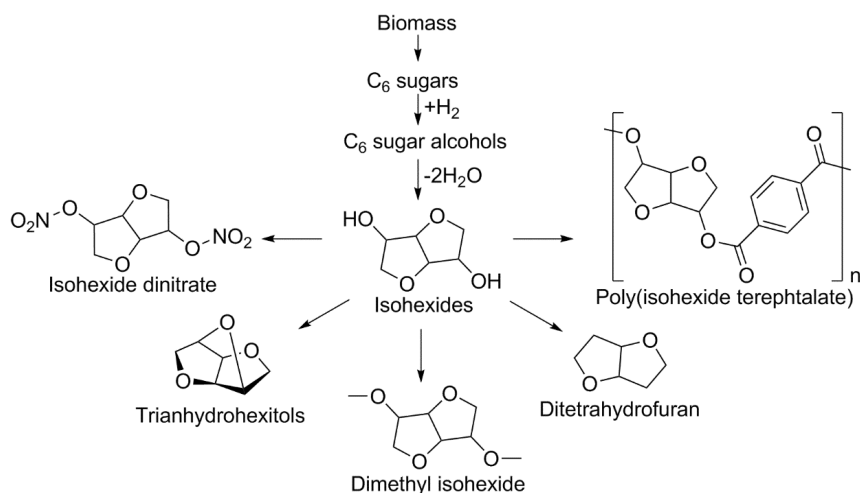


Figure 17 The conversion of biomass to isohexides and their further upgraded derivatives.^[8,47]

3.7.2 HYDROGENATION OF MONOSACCHARIDES

The hydrogenation of glucose to sorbitol with a heterogeneous ruthenium catalyst and H_2 as the hydrogen source has been proposed to proceed in the following fashion. Initially, H_2 molecules are solvated into the reaction solution with the monosaccharide (Figure 18).^[145,146] This is followed by the adsorption of H_2 onto ruthenium surface, whereupon each H-H bond breaks forming two H atoms on the surface of the catalyst (Step 1). After this, two alternative pathways have been suggested depending on whether the monosaccharide is in acyclic or cyclic form. The form of the monosaccharide determines how the oxygen atoms coordinate and interact with the ruthenium catalyst (Step 2). Next, the first hydrogen atom is transferred to the carbonyl carbon or to the anomeric carbon (Step 3). Subsequently, another H_2 molecule is adsorbed and split up on the surface of the catalyst; this is followed by a second hydrogen transfer to the appropriate oxygen atom of the substrate, forming sorbitol as the product (Step 4). The hydrogenation of other aldoses, such as mannose, idose and xylose, to corresponding sugar alcohols can be considered to proceed by in similar mechanism.

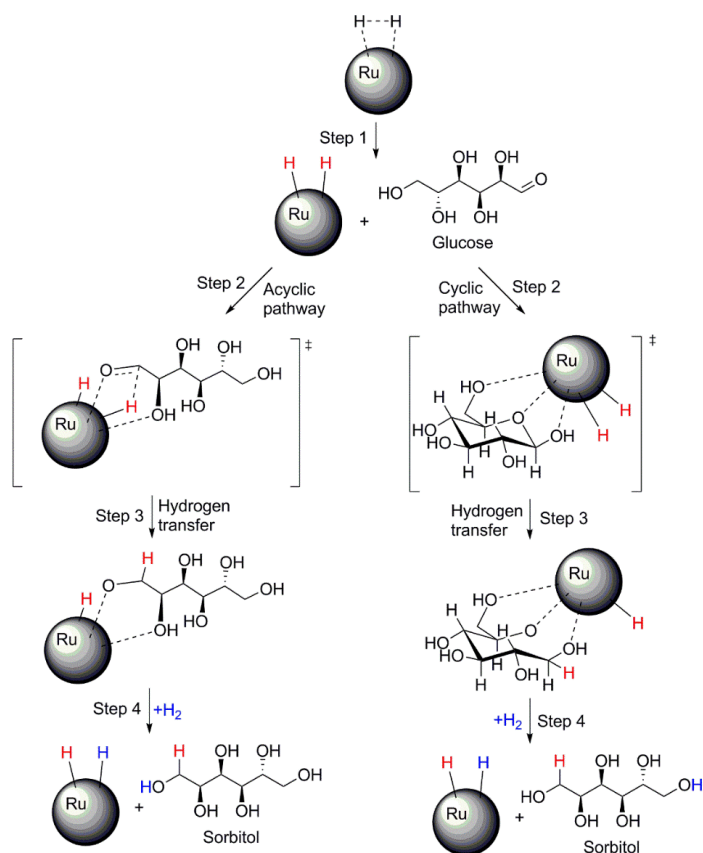


Figure 18 The proposed reaction mechanisms of glucose hydrogenation to sorbitol with a heterogeneous Ru-catalyst.^[145,146]

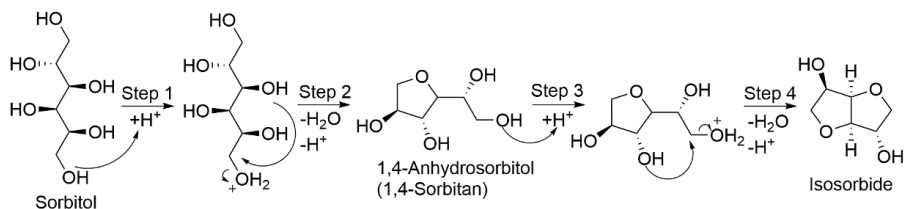
The heterogeneous hydrogenation of sugars has been studied with various different catalysts, including Ru-, Ni-, Co-, Pt-, and Pd-based catalysts on a plethora of different support materials combined with different promoters.^[20,30,147,148] Currently, Ru- and Ni-based are the most used catalysts in sugar hydrogenation, of which Ru-based catalysts have been found to be the most active.^[36,149] Also, ruthenium is more stable than nickel catalysts under the usual glucose hydrogenation conditions and no leaching of ruthenium catalysts has been reported. This is a highly desired attribute for hydrogenation catalysts, especially in medicinal and food applications.^[149] The hydrogenation of glucose to sorbitol can be combined with the hydrolysis of cellulose. The hydrolysis of the glycosidic bonds requires the use strong acids and some acidic support materials have been shown to facilitate this conversion as well, thus promoting the replacement of the homogeneous mineral acids with heterogeneous acids. In this context, the use of a heterogeneous Ru/NbOPO₄ dual catalyst in the conversion of cellulose to sorbitol generated a good yield of 69% of the sugar alcohol at 160 °C under 40 bars of H₂. In comparison, the use of 2.5 wt.% H₂SO₄ and Ru/C generated sorbitol in a moderate yield of 33% under similar reaction conditions.^[20,150] However, it should be noted that highest sorbitol yield was obtained after one hour with H₂SO₄, as opposed to the 24-hour reaction time required with the NbOPO₄ catalyst. Furthermore, the longer reaction times with H₂SO₄ generated anhydrosorbitols (sorbitans) and isosorbide as the main products through sorbitol dehydration. Consequently, it is logical to pursue the synthesis of isohexides directly from hemicellulose and cellulose by employing the same acid used in the hydrolysis of the polysaccharides in the dehydration of sugar alcohols.

3.7.3 DEHYDRATION OF SUGAR ALCOHOLS

The acid-catalyzed dehydration of sugar alcohols is a stepwise reaction that is commonly considered to proceed in S_N2 substitution mechanism.^[151] The first dehydration of C₆ sugar alcohols forms four different kind of dehydration products depending on the protonated hydroxyl group (Figure 19). For example, protonation of the sorbitol hydroxyl groups positioned at C1, C3, C4, and C6 and the subsequent cyclization through dehydration can form 1,4- and 3,6-anhydrosorbitols (Figure 19, Steps 1 and 2).^[152] These monoanhydrosorbitol intermediates can then undergo another protonation of suitable hydroxyl groups, followed by a second ring-closing dehydration to form the desired isosorbide (Steps 3 and 4). However, the first protonation and dehydration can also form the undesired 1,5- or 2,5-anhydrosorbitols, which cannot directly be converted to isosorbide. Kinetically 1,4-anhydrosorbitol is the most favored product from the first dehydration; however, the dehydration of 3,6-anhydrosorbitol to isosorbide is considerably faster than 1,4-anhydrosorbitol.^[151] The isomannide and isoidide are formed through similar dehydration of the corresponding hydroxyl groups.

Accordingly, the dehydration of xylitol forms 1,4- and 2,5-anhydroxylitols as products, of which 1,4-anhydroxylitol is the main product.^[141]

Reaction mechanism shown with the first protonation of C1 hydroxyl group



Other anhydrosorbitols occurring in the synthesis of isosorbide

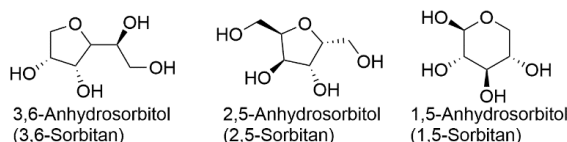


Figure 19 The conversion of sorbitol to isosorbide through two-fold dehydration.^[152]

The conversion of sorbitol to isosorbide can be conducted using different kinds of catalytic systems. For example, the dehydration of sorbitol using typical mineral acids H_2SO_4 , HCl , and H_3PO_4 in aqueous solutions, revealed that H_2SO_4 generates isosorbide in highest 77% yield at 135 °C in 20 hours.^[153] Moreover, the conversion of sorbitol to isosorbide has been achieved in excellent 95% yield in ZnCl_2 hydrate media with CuCl_2 as a cocatalyst, although high 24:2:1 (ZnCl_2 :sorbitol: CuCl_2) metal chloride to sorbitol ratios were used.^[152] In contrast, the use of heterogeneous dual-catalyst $\text{Ru}/\text{Dowex-H}$ catalyst in an aqueous solution generates isosorbide and anhydroxylitol in very good 85% and 95% yields from glucose and xylose, respectively.^[3] Even high temperature liquid water has been shown to facilitate the isosorbide formation from sorbitol in 57% yield in the absence of any additional acids.^[154] The dehydration of mannitol to isomannide has been shown to be more challenging than the dehydration of sorbitol. With the use of 0.1 M H_2SO_4 as a catalyst, isosorbide is formed in 21% yield at 170 °C in 10 minutes, whereas the dehydration of mannitol requires higher reaction temperature and longer reaction time, 180 °C and 20 minutes, to produce a similar 20% yield of isomannide.^[141] Although the dehydration of sugar alcohols can also be conducted using base and Lewis acid catalysts, these approaches restrict the synthesis of the isohexides to solely sugar alcohols or monosaccharides, due to their poor ability to cleave glycosidic bonds of the natural polysaccharides.^[151,155] Acidic catalysts allow multistep reactions, for example, the highly desired direct transformation of cellulose to isosorbide. Currently, the largest production unit has the capacity to produce 20000 tons of isosorbide annually from starch-based sorbitol.^[156] In this regard, highly

efficient and sustainable synthesis of isosorbide from inedible resources, such as lignocellulosic biomass, is still in high demand.

3.7.4 SYNTHESIS OF ISOSORBIDE FROM CELLULOSE

The studies on the synthesis of anhydro sugar alcohols from lignocellulosic polysaccharides have been mostly conducted in aqueous solutions with cellulose, due to availability of the substrate and the more facile conversion of the glucose to isosorbide than the conversion of mannose to isomannide. In theory, the combination of hydrolysis, hydrogenation, and dehydration of the polysaccharides is rather straightforward as the hydrolysis and the dehydration can be catalyzed with the same acid catalyst, and the hydrogenation requires a suitable catalyst and a hydrogen source. Accordingly, several studies have reported transformation of cellulose to isosorbide in rather good yields.^{[21,157–159],II} Similarly to the previously covered hydrogenation of glucose to sorbitol, due to their efficiency and resilience towards leaching, Ru-based catalysts are the most frequently used catalysts. Meanwhile, different acid catalysts have been employed in the reaction in combination with Ru-catalysts, such as homogeneous HCl and H₂SO₄ as well as heterogeneous Amberlyst 70, niobium phosphate and H₄SiW₁₂O₄₀.^{[21,157–159],II} The use of the mineral acids HCl and H₂SO₄ have been reported to generate isosorbide from MCC in 50% and 56% yields with 6 and 8 hour reaction times, respectively.^{[21],II} With the use of heterogeneous acids isosorbide can be produced in yields of 52–63% from cellulosic substrates, concurrently avoiding the drawbacks of the homogeneous acids.^[157–160]

Evidently, the conversion of cellulose to isosorbide can be achieved in very good yields. However, the deactivation and the stability of the heterogeneous hydrogenation catalysts has been a major problem in the synthesis of isosorbide from cellulose. It has been shown that the longer exposure times and higher temperatures accelerate the deactivation of the hydrogenation catalysts with both homo- and heterogeneous acids.^{[157],II} This is a significant problem in one-step reactions, as reaction temperatures of up to 215 °C are required to enable the dehydration of sorbitol and anhydro sugar alcohols to isosorbide, simultaneously subjecting the hydrogenation catalyst to the high temperatures. In this respect, splitting the reaction into two individual reaction steps enhances the lifetime of the catalyst considerably, as the hydrolysis and hydrogenation can be conducted at lower temperature.^{[160],II} After the first step, which is conversion of cellulose to sorbitol, the heterogeneous hydrogenation catalyst can be separated and the second step of the reaction can be conducted at higher temperature with the use of appropriate acid catalyst to ensure efficient dehydration to isosorbide. This sequential approach has been shown to enhance the recyclability of Ru-catalysts with H₂SO₄ and niobium phosphate as the acid catalysts.^{[160],II} A comparison of these acids shows that, with H₂SO₄, the Ru/C_{sulfonated} catalyst can be recycled even with lignin-containing cellulose as the substrate. Also the

total reaction time of 8 hours is significantly shorter than the corresponding 42 hours with niobium phosphate. On the other hand, the use of niobium phosphate as the support material ensures efficient regeneration of the hydrogenation catalyst through calcination.

The deactivation of the hydrogenation catalyst is a major problem in isosorbide synthesis, thus it has been extensively studied and multiple deactivation mechanisms and types have been identified.^[161,162] The deactivation of heterogeneous catalysts can be categorized into chemical, mechanical, and thermal types. Some of these types can be further divided into different mechanisms, for example, chemical deactivation includes poisoning and leaching. Mechanical deactivation can occur through, *e.g.*, fouling and crushing, while thermal degradation is a heat-inflicted loss of active catalyst sites. The most often reported deactivation mechanisms in the synthesis of isosorbide from cellulose are thermal degradation, poisoning, and fouling.

Thermal degradation usually appears through sintering of the catalyst nanoparticles during isosorbide synthesis, forming larger particles in size and accordingly losing the catalytic activity through reduced active surface area of the catalyst. In this matter, a study on the recycling of Ru/C conducted by Liang *et al.*^[21] revealed that, during the first run, the average size of the ruthenium nanoparticles had grown from 1.2 nm to 1.7 nm at 215 °C under 60 bars of H₂ in aqueous 0.1 M HCl solution. The lower product yields obtained in the following runs under identical reaction conditions were thought to arise from the enlarged ruthenium particles.

Poisoning and fouling are similar, commonly reported deactivation mechanisms. The deactivation arises through blocking of the active sites of the catalyst.^[161] In poisoning, the blocking agents are chemisorbed irreversibly on the surface of the catalyst, whereas in fouling, the blockage occurs in a physical manner, for example, covering the catalyst surface or by blocking the pores of the catalyst. In the one-pot conversion of cellulose to isosorbide with an H₄SiW₁₂O₄₀ acid catalyst and Ru/C at 210 °C, the hydrogenation catalyst was reported to deactivate through carbon precipitating on the surface of the catalyst, explaining the increased mass of the catalyst after the reaction.^[159] Yamaguchi *et al.*^[157] proposed similar deactivation by carbon fouling on Ru/C at various temperatures (170-190 °C), after ruling out deactivation through sintering and leaching of ruthenium. Recently, an acidified carbon support material has been shown to increase the recyclability of the Ru-based catalyst in the two-step conversion of cellulosic substrates to isosorbide.^{II} The enhanced recyclability is a result of the more hydrophilic surface of the support, which is thought to reduce the adsorption and fouling by decreasing the CH- π hydrogen bonding of the fouling species and the hydrophobic parts of the surface of the catalyst. Moreover, these acidified RuO_x/C_{sulfonated} catalysts have been shown to be recyclable even with lignin containing substrates, providing high product yields in at least four consecutive runs.

3.7.5 OVERVIEW OF THE REACTIONS

Anhydro sugar alcohols can be produced from various poly- and monosaccharide substrates through hydrolysis, hydrogenation, and dehydration. The anhydro sugar alcohols, such as isosorbide, isomannide, and anhydroxylitol, can be utilized in various different polymer, medicinal, and fine chemical applications. The synthesis of anhydro sugar alcohols has been achieved in high yields from monosaccharides and corresponding sugar alcohols using efficient Ru-based hydrogenation catalysts and acidic dehydration catalysts. Despite the good yields from monosaccharides, in order to synthesize the anhydro sugar alcohol sustainably, the residual lignocellulosic materials from paper and pulp and agricultural industries should be used as the feedstocks.

The synthesis of anhydro sugar alcohols from polysaccharide sources have been studied mainly with cellulose and its conversion to isosorbide, due to the versatility of the product, abundance of the substrate, and the relatively facile conversion of sorbitol to isosorbide. The one-pot conversion of cellulose to isosorbide provides good product yields in short reaction times with both homo- and heterogeneous acids, but unfortunately, the reaction conditions cause deactivation of the valuable hydrogenation catalyst. Accordingly, two-step reaction setups have been devised and significantly enhanced recyclability has been obtained, even with the lignin-containing cellulosic substrate.

Deactivation of the hydrogenation catalyst can be caused by a variety of different mechanisms, for example, leaching, fouling, poisoning, and thermal degradation. Although the causes of these mechanisms are quite well known, no inclusive solution has been developed to resolve this problem as the reaction conditions between reaction setups might differ significantly from each other and thereby the deactivation mechanisms needs to be identified and assessed case-by-case. Furthermore, it has been shown that deactivation of the hydrogenation catalyst cannot be avoided simply by careful optimization of the reaction conditions, thus development of more tolerant and robust catalysts is needed. In this respect, there have been a couple of pioneering publications, which state that the catalytic activity of the hydrogenation catalyst can be significantly enhanced with the use of two-step systems in combination with modified hydrogenation catalysts or efficient regeneration methods.^{[160],II}

Although some of the problems concerning the synthesis of anhydro sugar alcohols from polysaccharides have been solved, there is still need for development of the reaction procedures. For example, the conversion of cellulose to isosorbide in a reasonable time requires high temperatures, homogeneous acids, and high H₂ pressures. The replacement of the homogeneous acids with heterogeneous ones would reduce the formed waste and furthermore it would ease the separation of the products from the solution. The increased solubility of H₂ in hot aqueous solutions or the use of a transfer hydrogenation setup could help to reduce the required high pressures.

3.8 UPGRADING OF TERPENOIDS

3.8.1 GENERAL ASPECTS

Besides polysaccharides and lignin, plants and trees produce terpenes for various purposes. These versatile organic compounds contain different functionalities, for example, C=C double bonds, hydroxyl groups, aldehydes, and ketones, which through valorization could be utilized in fine chemical, fuel and polymer applications. One possibility for the upgrading is the Brønsted- or Lewis acid-catalyzed dehydration of the terpene alcohols to olefins, of which the Lewis acids are more preferred due to the disadvantages of Brønsted acids. Terpene alcohols are a class of terpenoids, which include an additional hydroxyl group in the terpene skeleton. The effects of both homo- and heterogeneous Lewis acids, such as Re_2O_7 , $\gamma\text{-Al}_2\text{O}_3$, and metal triflates, have been studied in the conversion of alcohols and monoterpene alcohols to olefins and they have been shown to be more efficient than Brønsted acids.^[5,46,163] Typical examples of monoterpene alcohols are menthol, linalool, and α -terpineol (Figure 20), which can be found in plants and isolated as essential oils, such as tea tree oil. Despite the current modest use of terpenes as scents and fragrances, the dehydration of terpene alcohols would provide a wide set of olefin products in addition to the existing natural terpenes. These biomass-based olefins have already been considered as interesting substrates in the development of biopolymers.^[9,44] In addition to alcohols, terpenoids may contain other functional groups as well, such as esters, ether, ketones, and aldehydes that can be readily removed, thus widening the substrate library for bio-olefin synthesis even further. As an example, the hydrogenation of citral forms primary unsaturated alcohols products geraniol and nerol.^[164]

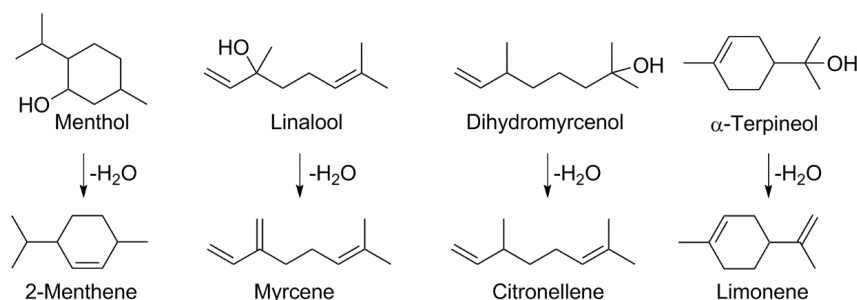


Figure 20 Example structures of different monoterpene alcohols and their dehydration products.

3.8.2 DEHYDRATION OF TERPENE ALCOHOLS

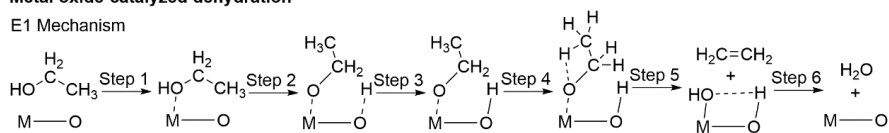
Two different elimination mechanisms, E1 and E2, depending on the interactions between substrates and catalyst, have been suggested for the metal oxide-catalyzed alcohol dehydration.^[165] The first step of the E1

mechanism, commonly considered as the Brønsted acid pathway, is adsorption of the alcohol onto the metal site of the catalyst (Figure 21, Step 1). After this, the alcohol undergoes the formation of alkoxide through O-H bond cleavage, followed by proton transfer to the basic oxygen site of the catalyst (Steps 2 and 3). The reaction proceeds with nucleophilic attack of the alkoxide oxygen at the β -hydrogen, forming metal hydroxide and alkene, which is then desorbed from the catalyst's surface (Steps 4 and 5). The catalyst is restored to its original state by dehydration, involving the hydroxide at the acid site and the neighboring proton at the base site (Step 6). The E2 mechanism is also initiated by the adsorption of the alcohol onto the acidic metal site of the catalyst (Step 1). This is followed by β -hydrogen abstraction by the base site oxygen of the catalyst, and desorption of the formed alkene (Steps 2 and 3). The catalytic cycle is completed by the dehydration of the metal oxide catalyst, similarly to the E1 mechanism (Step 4). Both of the elimination mechanisms have been reported occur, the dehydration of ethanol with γ - Al_2O_3 has been proposed to favor the E2 mechanism, as the adsorption of the alcohol is stronger at Lewis-acidic sites than at Brønsted sites.^[163] The use of homogeneous methyltrioxorhenium has been proposed to facilitate the dehydration by mechanism resembling the E1 pathway.^[166]

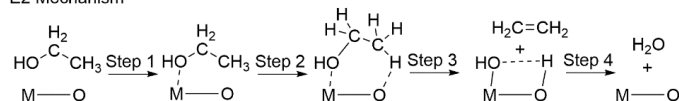
The metal triflate-catalyzed dehydration mechanism has been mainly studied under HDO reaction conditions with model alcohols forming alkanes as the products, due to the reductive environment.^[46] The dehydration of alcohols with use of homogeneous metal triflates catalysts has been proposed to proceed in the following fashion in non-reactive reaction media. First, the metal triflate is coordinated to the alcohol oxygen (Figure 21, Step 1). Next, the alcoholic C-O bond is cleaved, forming metal triflate hydroxide; simultaneously the β -hydrogen is transferred to metal triflate hydroxide, forming a neutral water ligand (Steps 2 and 3). The catalytic cycle is completed

Metal oxide-catalyzed dehydration

E1 Mechanism



E2 Mechanism



Metal triflate-catalyzed dehydration

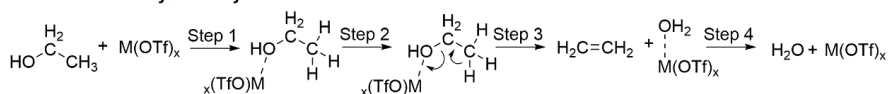


Figure 21 Proposed mechanisms for metal oxide and metal triflate-catalyzed dehydrations.^[46,165]

with the dissociation of the water from the metal triflate (Step 4). Despite their great potential as dehydration catalysts, reports dealing with metal triflate-catalyzed monoterpene alcohol dehydration to olefins are sparse.^{III}

The drawbacks of mineral acid catalysts have resulted in a change of focus in the catalyst development from Brønsted acid catalysts to homo- and heterogeneous Lewis acid catalysts. Different metal oxide catalysts, for example, tungstated zirconia and rhenium oxides, have been found to be effective catalysts for dehydration of alcohols to olefins.^[167,168] Rhenium oxides have been discovered to be especially efficient dehydration catalysts. In fact, the dehydration of terpene alcohols have been shown to be more efficient and selective using Re_2O_7 than H_2SO_4 .^[5] For example, when α -terpineol was dehydrated using Re_2O_7 the olefin products, limonene, and terpinolene, were formed in >99% yield at 100 °C in just 45 minutes using 0.5 mol.% catalyst loading with toluene as the solvent. Yet, the use of H_2SO_4 generated olefins in the yield of 95% under similar reaction conditions, but with 2.5 mol.% catalyst loading. Similarly, the use of tea tree oil as substrate in the Re_2O_7 -catalyzed dehydration of terpene alcohols produces quantitative conversion of terpene alcohols to terpenes in just 30 minutes at 100 °C, while the use of H_2SO_4 requires 3 hours for the conversion. Despite the excellent yields with Re_2O_7 , the catalyst is partially soluble in the reaction solution, which results in partial loss of the catalyst and deteriorating yields in the recycling experiments. The solubility is suspected to be caused by the reaction of the catalyst and water side product, forming HReO_4 .^[5] The higher oxidation state and the resulting higher Lewis acidity of the metal atoms increases the dehydration activity through enhanced binding of the metal site to the electrons of the hydroxyl oxygen.^[5] This stronger interaction weakens the C-O bond by lowering the electron density, thus facilitating the dehydration of the substrate.

In addition to the metal oxide catalysts, water stable metal triflates, such as $\text{Cu}(\text{OTf})_2$, $\text{Fe}(\text{OTf})_3$, and $\text{Hf}(\text{OTf})_4$, have emerged as interesting dehydration catalyst candidates.^{[146,169].III} Similarly to Re_2O_7 , $\text{Cu}(\text{OTf})_2$ has been shown to generate alkene products from alcohols more efficiently than H_2SO_4 .^[169] The dehydration of 3-methylpentan-3-ol with $\text{Cu}(\text{OTf})_2$ and H_2SO_4 formed alkenes in yields of 92% and 48%, respectively. The catalytic activity of the metal triflate catalysts has been shown to increase with increasing Lewis acidity and oxophilicity of the central metal under solvent-free conditions.^{III} In addition, triflate anions increase the Lewis acidic character of the central metal through their electron withdrawing ability and, as a result, more efficient dehydration is achieved when compared to salts with electron-donating anion, such as metal chlorides.^{[170].III} This is an interesting prospect, as the use of electron withdrawing triflate anions with abundant transition metals, such as iron, aluminium, and titanium increases the catalytic activity and it enables their use in dehydration of terpene alcohols.^{III} In this study, the impact of catalyst's calculated Lewis acidity, oxophilicity and used anion on catalytic activity were highlighted, when 2-octanol was dehydrated to octenes with $\text{Hf}(\text{OTf})_4$, FeCl_3 , and $\text{Fe}(\text{OTf})_3$. The use of FeCl_3 did not produce octenes, whereas with $\text{Fe}(\text{OTf})_3$

30% yield was obtained and the most efficient and oxophilic Hf(OTf)₄ produced an impressive 93% octenes yield under the same reaction conditions. Accordingly, the triflate salts have been applied to monoterpene alcohol dehydration. For example, dihydromyrcenol can be converted to olefins in isolated yields of 82% and 84% using Fe(OTf)₃ and Hf(OTf)₄, respectively, under solvent free conditions using 0.5 mol.% catalyst loading. The conversion of tea tree oil to terpenes was achieved in 53 wt.% isolated yield using Fe(OTf)₃ as the catalyst in 1 hour at 130 °C.

Although the aforementioned Lewis acids are efficient dehydration catalysts, they produce different isomer mixtures of the olefins as products, similar to H₂SO₄.^[5,169] For example, the dehydration of linalool with Re₂O₇ generated limonene, terpinolene, 2,6-dimethyloctatrienes, *p*-cymene, and γ -terpinene in yields of 43%, 22%, 32% and 2% (combined yield of *p*-cymene and γ -terpinene), respectively. Corresponding yields with H₂SO₄ were reported to be 20%, 25%, 11% and 56% (combined yield of *p*-cymene and γ -terpinene). Also, formation of isomers was found to occur with Fe(OTf)₃ and Hf(OTf)₄ catalysts, as the dehydration α -terpineol generates limonene, α -terpinolene, α -terpinene, and γ -terpinene as products in the corresponding ratio of 50:38:7:7, respectively.^{III} The formation of olefin mixtures with the present catalysts underlines the need for new more selective dehydration catalysts and systems.

In addition to conversion of monoterpene alcohols to olefins, metal triflates are reported to catalyze the cleavage of ester and ether bonds.^[171,172] For example, the direct cleavage of the alkoxy C-O bond of octyl acetate generated octenes in 68% and 80% isolated yields with Fe(OTf)₃ and Hf(OTf)₄ catalysts, respectively, under solvent-free conditions at 180 °C in 24 hours.^{III} Dioctyl ether, on the other hand, can be converted to octenes only with Hf(OTf)₄ through hydrolysis of the ether C-O bond to alcohols and their subsequent dehydration, generating a modest 29% yield of octenes at 180 °C in 24 hours. Astonishingly, tandem La(OTf)₃- and Pd/C-catalyzed system has been shown to efficiently promote the hydrogenolysis of ether and ester bonds from acetylated lignin model compound, resulting in quantitative conversion and good products yields.^[171] This catalytic activity of metal triflates could prove to be helpful in the conversion of ether- and ester-containing terpenes as well as in the upgrading of other biomass-based ethers and esters. In general, the reactivity order of hydroxyl groups toward dehydration decreases in the order of *tert*-alcohols>*sec*-alcohols>>*prim*-alcohols, and with non-benzylic alcohols allylic>aliphatic>homoallylic, following the stability of the carbocation.^[5]

3.8.3 OVERVIEW OF TERPENE UPGRADING

The wide library of terpenes presents an interesting opportunity to produce biomass-based olefins and other defunctionalized bioproducts for the needs of industry. For example, monoterpene alcohols can be converted to biomass-based olefins through acid-catalyzed dehydration. The conversion has been

found to be more efficient with Lewis acid catalysts than the studied Brønsted acids. The obtained olefins are interesting starting materials for the production of biopolymers, and they can be used as the replacements for petroleum-based substrates.^[44] Currently, terpene alcohols, aldehydes, and ketones containing essential oils are produced in large quantities mainly for pharmaceutical, cosmetic, and food industry purposes. These essential oils, such as tea tree oil and citronella, could serve as feedstocks for the biomass-based olefin synthesis. In addition to monoterpene alcohols, different biomass-based esters and ethers could also be utilized as feedstocks for the synthesis of olefins.

The conversion of terpenoids to olefins has not been studied as extensively as the conversion of lignocellulosic products to furfurals or isosorbide. Despite this, good preliminary results have been obtained with rhenium oxide and metal triflate catalysts in the synthesis of olefins from various biomass-based alcohols. However, there are problems concerning the catalysts in the dehydration of alcohols; for example, both the recycling and separation of the catalyst has proven to be challenging. The present dehydration methods of monoterpene alcohols form multiple isomers as the reaction products. Therefore, new catalysts and reaction environments promoting the product selectivity, catalyst recyclability and increased reactivity of the more passive alcohols, as well as other functionalities, should be developed.

4 RESULTS AND DISCUSSION

All the related materials and methods as well as the rest of the experimental details, can be found from the original articles. This section will cover the main findings of the author's publications **I-III**.

4.1 HYDRODEOXYGENATION OF FURAN COMPOUNDS TO CORRESPONDING ALKANES (PUBLICATION I)

The interest in defunctionalization of biomass-based compounds has increased drastically during the last decade. The complete defunctionalization of these oxygen-rich substrates could provide a sustainable source of liquid fuels, fine chemicals, and solvents. However, more efficient procedures for biomass conversion are needed in order to replace petroleum feedstocks. In this work, we developed a one-step HDO reaction setup for the synthesis of branched alkanes from biomass-based furans using Pd/C as hydrogenation catalyst and metal triflates as deoxygenation catalysts. The previous works in this field have employed two-step reactions, resulting in longer reaction times and more complicated execution.^[112,129] The substrates for this study were synthesized from furfural and HMF with aldol condensation using MIBK as the condensation partner. The condensation product obtained from HMF will be denoted as **1** and the furfural-based substrates as **2**. The corresponding alkanes will be denoted as **3** and **4**, respectively (Figure 22).

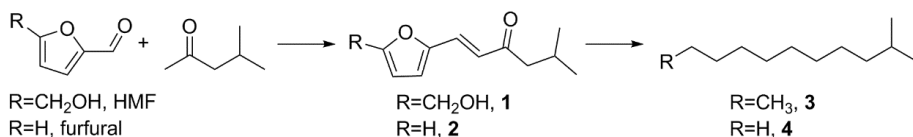


Figure 22 Reaction pathway for the conversion of biomass-based furans to branched alkanes.

The study began with deoxygenation catalyst screening using biomass-based furan **2** as the substrate (Table 1). The screening was conducted using different deoxygenation metal catalysts and AcOH as the solvent. The deoxygenation catalysts were mostly chosen to be metal triflates as they had been reported to work in previous publications.^[112,129] The catalyst screening revealed that Eu(OTf)₃ generated 2-methyldecane in the highest yield of 73%. Compared to other lanthanides, Eu³⁺ has high Lewis acidity and low oxophilicity, which could explain the high catalytic activity. In general, the triflate salts generated better reaction outcomes than the metal chlorides. The triflate anion is an electron withdrawing anion, inducing higher Lewis acidity

in the metal cation. As a result of the catalyst screening, we continued the study with Eu(OTf)₃ as the deoxygenation catalyst.

Table 1 The results of deoxygenation catalyst screening in AcOH.^a

Entry	Deoxygenation catalyst	4 yield ^b
1	La(OTf) ₃	53
2	Eu(OTf) ₃	73
3	Fe(OTf) ₃	35
4	Y(OTf) ₃	21
5	Sc(OTf) ₃	49
6	Nd(OTf) ₃	59
7	Hf(OTf) ₄	18
8	EuCl ₃	2
9	FeCl ₃	7
10	LaCl ₃	9
11	-	0
12	HOTf	49

^a Reaction conditions: 5.7 mmol of **2**, 0.4 mol.% of Pd/C (5 wt.%), 15 mol.% of deoxygenation catalyst, 16 h, 200 °C, 40 bar H₂ (at room temperature) and AcOH as solvent; ^b Yields were obtained with gas chromatograph equipped with flame ionization detector (GC-FID) and calibration curves.

As alternative deoxygenation mechanisms had been proposed using different solvents, the solvent effect on the reaction outcome was studied.^[46,128] The deoxygenation in AcOH proceeds through acetoxylation of the hydroxyl, followed by the removal of the acetate group due to the effect of the metal triflate, forming an alkene and acetic acid.^[128] The formed alkene is then hydrogenated to form final alkane product. In nonreactive solvents, such as octane, deoxygenation is reported to proceed in direct metal triflate-catalyzed cleavage of the hydroxyl group, followed by hydrogenation of the unsaturated C=C double bonds.^[129]

In the solvent screening, we used AcOH, octane and EtOAc and their mixtures with Eu(OTf)₃ as the deoxygenation catalyst. The use of AcOH resulted in 11% yield of alkane with **1** as the substrate. However, the alkane yield was even lower, 3%, when octane was used as the solvent. This was due to the low solubility of the substrate in the nonpolar solvent. Mixing AcOH and EtOAc with octane increased the solubility and resulted in higher 40% and 65% **3** yields, respectively. The use of EtOAc as the sole solvent resulted in the highest **3** yield of 78%. Moreover, with **2** as the substrate, the use of octane and EtOAc as solvents resulted in 86% and 98% yields of **4**, respectively. Evidently, the deoxygenation through acetoxylation-deacetylation in AcOH is not as efficient as the direct deoxygenation in EtOAc and octane. Based on the

experiments, EtOAc was selected as the solvent for further studies. It should be noted that, under solvent-free reaction conditions 53% yield of **4** could be obtained.

The catalytic performance with the time-on-stream was investigated under the optimal reaction conditions. The formation of the corresponding alkane was found to be faster with **2** than with **1**. Using **2**, the reaction time could be reduced from 16 hours to 6 hours without loss of **4** yield (Figure 23). In comparison, the use of **1** as the substrate resulted in the formation of **3** at a significantly slower rate and longer reaction time had to be employed. The best **3** yield of 90% was obtained in 24 hours. Our NMR studies revealed that this slowed formation of alkane was due to the presence of the primary hydroxyl group, which is known to be more challenging to remove than the secondary and tertiary hydroxyl groups.^[46,173] Throughout the time-on-stream studies, full conversion of the substrates was detected. This was ascribed to the rapid hydrogenation of the unsaturated bonds, demonstrating that the rate-determining step is the dehydration under these reaction conditions.

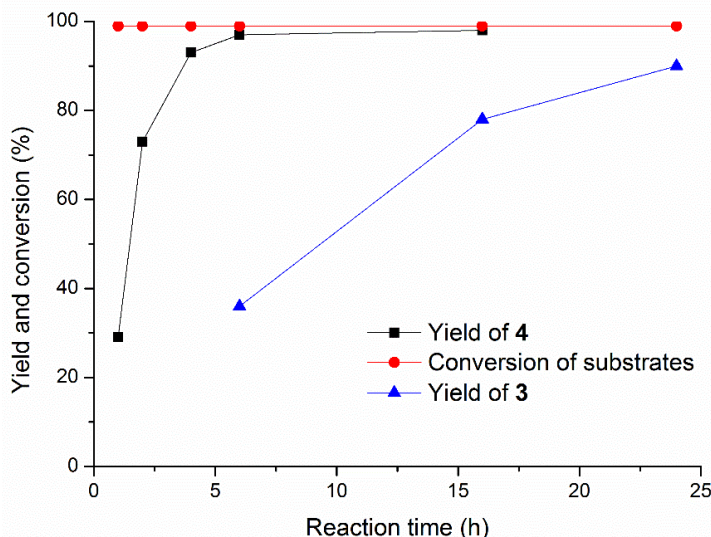


Figure 23 The HDO of **1** and **2** to **3** and **4** results as a function of time-on-stream.

Next, we focused on the recycling of the catalysts with **2** as the substrate. The recycling proved to be mediocre at best, as good alkane yields could be obtained only in the first two runs in octene. Although the yield of **4** was drastically reduced from 80% in second run to 20% in the third run, full conversion of substrate was still detected. Quantitative conversion was achieved through hydrogenation, and apparently, the poor recyclability arises from the deactivation of the deoxygenation catalyst $\text{Eu}(\text{OTf})_3$, presumably through poisoning.

In order to establish the reaction pathway of the $\text{Eu}(\text{OTf})_3$ and Pd/C -catalyzed one-step HDO reaction in EtOAc, mild temperature reactions were conducted with **1** and **2**. At 100 °C, it was found that both the substrates were, in fact, hydrogenated to THF compounds instead of furan ring opening. At higher temperatures the hydroxyl groups were removed with $\text{Eu}(\text{OTf})_3$ -catalyzed deoxygenation, which was followed by hydrogenation of the formed $\text{C}=\text{C}$ double bonds. A similar direct deoxygenation pathway has been proposed for the $\text{Hf}(\text{OTf})_4$ -catalyzed two-step HDO reaction of furans to alkanes.^[46,129] According to our NMR studies, the oxygen functionalities are removed in the following order: 1) secondary hydroxyl group, 2) ring-opening of the cyclic ether and subsequent removal of the forming secondary hydroxyl group, and 3) primary hydroxyl group (Figure 24).

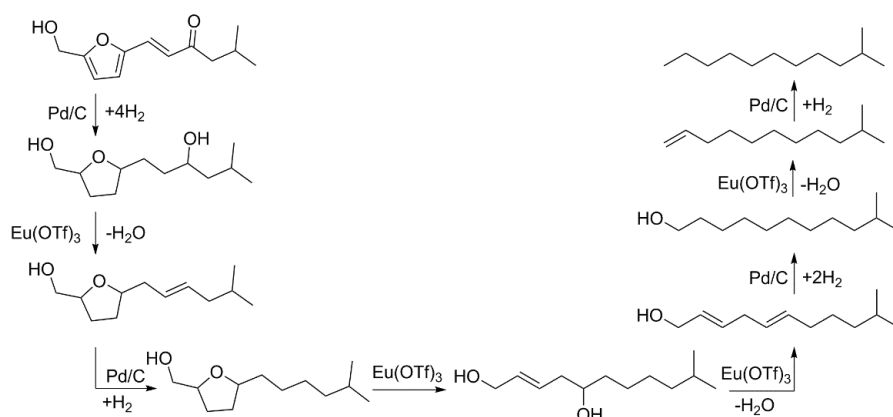


Figure 24 Proposed reaction mechanism of $\text{Eu}(\text{OTf})_3$ and Pd/C -catalyzed HDO in EtOAc.

In this study, a high yield one-step HDO reaction to convert biomass-based furan compounds to corresponding alkanes in over 90% yields was developed. We found that $\text{Eu}(\text{OTf})_3$ is the most efficient deoxygenation catalyst, and that the deoxygenation activity is enhanced when the strongly electron-withdrawing triflate anion is used. The solvent has a significant effect on the reaction mechanism and the outcome; AcOH promotes the deoxygenation through an acetoxylation-deacetylation pathway, while the reaction in octane and EtOAc proceeds through direct dehydration. The best solvent was found to be EtOAc with both **1** and **2** as substrates. According to the mechanistic studies, the long reaction times required for the conversion of **1** to alkane was due to the presence of the primary hydroxyl group. Under the optimized reaction conditions with the use of $\text{Eu}(\text{OTf})_3$ and Pd/C as the catalysts, **3** and **4** were obtained in excellent yields of 90% and 98%, respectively.

4.2 CONVERSION OF CELLULOSE TO ISOSORBIDE (PUBLICATION II)

The synthesis of biomass-based platform chemicals, such as isosorbide, directly from lignocellulosic material is highly sought after. However, the isosorbide synthesis from cellulose has suffered greatly from the ineffective systems and rapid deactivation of the expensive hydrogenation catalysts. The deactivation is caused mainly by fouling and poisoning of the catalyst as well as thermally induced physical changes, for example sintering. Consequently, we designed an efficient two-step system that enables the recycling of the hydrogenation catalyst, by minimizing the thermal impact on the catalyst (Figure 25). More importantly, we developed a ruthenium-based hydrogenation catalyst with more tolerance towards lignin and other fouling agents than the commercial Ru/C. The reactions were conducted using MCC, dissolving pulp (DP, obtained from Stora Enso), and bagasse pulp (BP, 95.37 wt.% cellulose and 4.63 wt.% lignin, obtained from Stora Enso) as substrates.

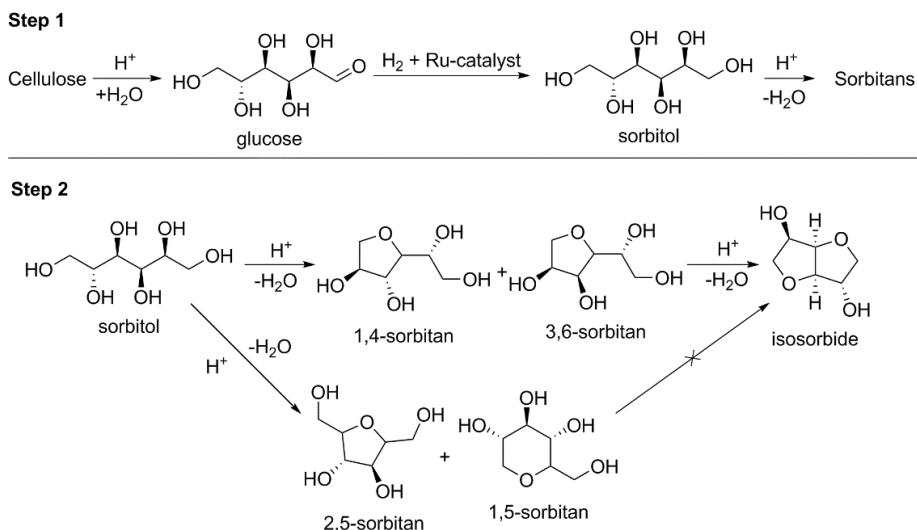


Figure 25 Two-step reaction pathway for the conversion of cellulose to isosorbide.

Initially, we compared optimized one- and two-step approaches for the synthesis of isosorbide and catalyst recyclability using commercial Ru/C as the hydrogenation catalyst (Table 2). MCC, BP, and DP were used as substrates without any purification or drying treatments. The catalyst studies showed that the most efficient catalysts were H_2SO_4 and Ru/C, and they were used in the following experiments. The one-step reaction setup ensured rapid conversion of cellulose to isosorbide in good 51% yield. In comparison, the two-step approach provided slightly higher 52-54% isosorbide yields in a total reaction time of 8 hours under the optimized reaction conditions. The biggest

drawback of the one-step system was the non-existent recyclability of the hydrogenation catalyst, as it underwent complete deactivation in the first run. Despite the longer overall reaction times, the two-step system enabled recycling of the Ru/C catalyst with the lignin-free cellulosic substrates. The catalyst was separated by filtration after the first hydrolysis and hydrogenation step. After this, the second step was conducted with clear filtrate at elevated temperature to ensure the complete dehydration of the sorbitol and sorbitans to isosorbide.

Table 2 Comparison of the optimal one- and two-step reaction setups in the isosorbide synthesis.

One-step setup ^a			Two-step setup ^b		
Substrate	Catalyst	Isosorbide yield (%) ^c	Substrate	Catalyst	Isosorbide yield (%) ^c
MCC	Ru/C	51	MCC	2 nd use Ru/C	54
BP	Ru/C	50	BP	2 nd use Ru/C	54
DP	Ru/C	50	DP	2 nd use Ru/C	52

^a Reaction conditions: 1.18 mmol of cellulose, 0.5 M H₂SO₄ (aq) 30 ml, 220 °C, 40 bar H₂, 2 hours and 0.02 mmol of Ru (5 wt.% Ru/C); ^b Reaction conditions: 1.18 mmol of cellulose, 0.5 M H₂SO₄ (aq) 30 ml; first step: 170 °C, 20 bar H₂, 2 h and 0.02 mmol of second run Ru/C. The second step is conducted with the filtrate from the catalyst filtration; second step: 200 °C, 40 bar H₂, 6 h; ^c The yields were obtained with high-performance liquid chromatograph equipped with refractive index detector (HPLC-RID) using calibration curves.

The recyclability studies of the commercial Ru/C catalyst were conducted under the optimized first step reaction conditions of the two-step setup with different cellulosic substrates (Figure 26). The experiments were conducted in four consecutive runs, where the catalyst was isolated and gathered through filtration, washed with milli-q water and dried in an oven (85 °C) for the following run.

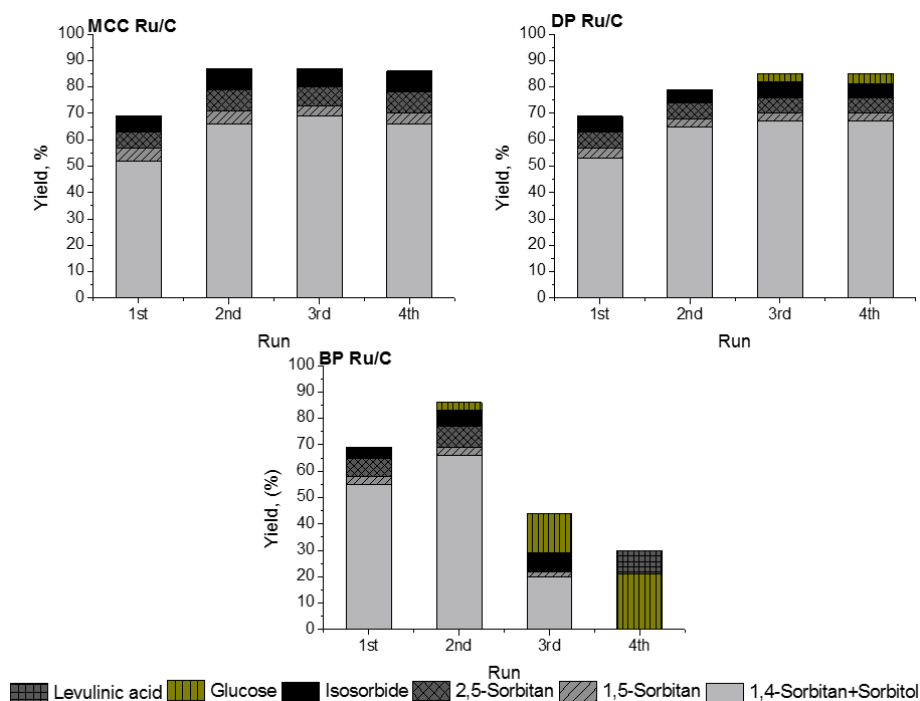


Figure 26 The outcome of the Ru/C recycling studies under the optimal first step reaction conditions with different cellulosic substrates.

The recycling investigations revealed that the activity of the commercial Ru/C was retained for four runs with the lignin free cellulosic substrates MCC and DP. This was a significant improvement compared to the one-step setup, where the catalyst was deactivated during the first run. However, the activity of the Ru/C collapsed in the third run with BP as substrate, presumably through fouling by lignin or by other compounds. As a result of the deactivation, LA and FA were formed through the glucose isomerization-dehydration-rehydration cascade reaction.

Surprisingly, the recycling experiments showed a significant increase of 1,4-sorbitan and sorbitol yields in the second run, and they were detected in combined yields of 66% with MCC, 65% with DP and 66% with BP. Whereas the yields after the first runs were 52% with MCC, 53% with DP and 55% with BP. To find out if the increased yields were caused by the adsorption and desorption of the products on the catalyst, we subjected the once-used Ru/C catalyst batch to similar reaction conditions without any cellulosic substrates. It turned out that only 3% of the products were detected from the solution after heating, and thus, the adsorption-desorption phenomenon could not explain the elevated yields. In this light, it seemed likely that the catalyst undergoes chemical modification under these conditions. The Boehm-titration verified this assumption, as the amount of strong acid sites on the surface of the catalyst was almost doubled during the first run. The increase of the strong

acid sites is known to increase the hydrophilicity of the catalyst surface, and in turn it enhances the accessibility of the hydrophilic molecules on the surface of the catalyst, possibly explaining the higher yields in the second runs.^[174,175] Furthermore, we hypothesized that the hydrophilicity could increase the recyclability of the catalysts through reduced hydrophobic interactions and CH- π hydrogen bonding between the surface of the catalyst and fouling agents.^[176,177]

The study was continued by investigating the effect of hydrophilicity of the hydrogenation catalyst on its recyclability. Since the lignin-free cellulosic substrates are not viable options for industry, a preferred lignocellulosic substrate, BP, was used in the experiments. A set of different catalysts was prepared by first sulfonating the support material, activated carbon, with different H₂SO₄-treatments. The support materials were treated with 10 M or concentrated H₂SO₄ for 0.5 or 3 hours at 110 °C. The sulfonation was followed by two different heat-treatments (2 h, 400 °C) reductive and oxidative, which generated metallic (denoted as Ru/C_{sulfonated}) and partially oxidized ruthenium nanoparticles (denoted as RuO_x/C_{sulfonated}), respectively.

The reductive treatment of the Ru/C_{sulfonated} catalysts reduced the amount of strong acid sites from 314-447 $\mu\text{mol/g}$ of the sulfonated support materials down to 233-333 $\mu\text{mol/g}$. In comparison, the amount of the strong acid sites in RuO_x/C_{sulfonated} catalysts were 325-425 $\mu\text{mol/g}$. This observation was in line with the X-ray photoelectron spectroscopy (XPS) results showing higher relative amount of carboxylic acids in the oxidized catalysts than in the reduced catalysts. The difference in the amounts of strong acid sites can be explained by the different heating treatments in the catalyst preparation. The reductive treatment was conducted under a forming gas (5% H₂ / 95% N₂) atmosphere all the time. According to the literature, carboxyl acid groups are decomposed at 200 °C and sulfonic acids at around 350 °C under an inert atmosphere, thus explaining the reduced strong acid sites.^[178,179] The RuO_x-catalysts were reduced similarly; however, after this, the oven was cooled to 290 °C and the atmosphere was changed to air and cooled to room temperature. This oxidative treatment generates carboxylic acid functionalities on the surface of the carbon support, thus restoring some of the decomposed strong acid sites.^[180]

The recyclabilities of the new Ru/C_{sulfonated} and RuO_x/C_{sulfonated} catalysts were then studied using BP as the substrate (Figure 27). The recycling experiments were conducted under the same optimized first step reaction conditions as with the commercial Ru/C (170 °C, 2 h, 20 bar H₂, 0.5 M H₂SO₄).

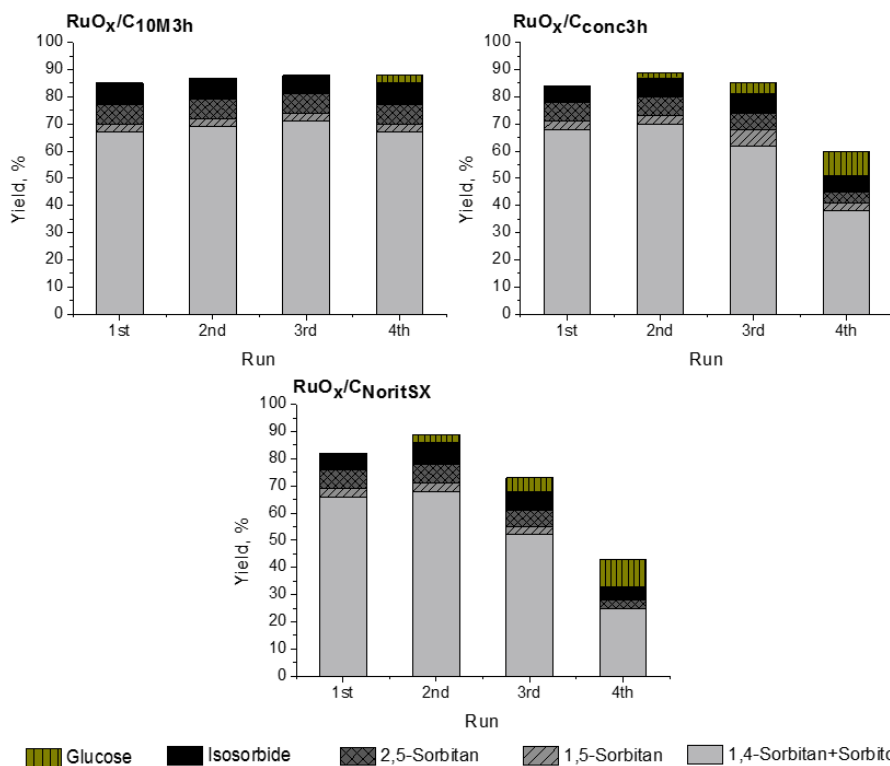


Figure 27 The outcome of the RuO_x/C_{sulfonated} recycling studies under the optimal first step reaction conditions with BP as the substrate.

The recycling studies conducted with the new catalysts revealed that the Ru/C_{sulfonated} catalysts were not as efficient or recyclable as the RuO_x/C_{sulfonated} catalysts, and in fact, the performance of the metallic sulfonated catalysts was inferior to the commercial Ru/C. However, the RuO_x/C_{sulfonated} exhibited significantly enhanced recyclability compared to the other hydrogenation catalysts. Although the non-acidified reference catalyst Ru/C_{NoritSX} underwent deactivation after the second run, it was not as severe as with the commercial Ru/C. The use of the acidified support material in the hydrogenation catalysts enhanced the recyclability even further. RuO_x/C_{10M3h} generated the best reaction outcome and, more importantly, it was recyclable in four consecutive runs without losing its activity with the lignin-containing substrate BP. The difference in recyclability between the acidified catalysts was thought to arise from the different amounts of sulfonic acid functionalities between the catalysts. The catalysts treated with concentrated H₂SO₄ are assumed to contain more sulfonic acid functionalities than the ones treated with 10 M H₂SO₄. It has been reported that sulfonic acid functionalities are more susceptible to hydrolysis than carboxylic acids under high temperatures in aqueous solutions, thus reducing the hydrophilicity of the catalyst's surface

and resulting in reduced recyclability.^[178] In this respect, carboxylic acids should be preferred over the sulfonic acids.

Next, using the best RuO_x/C_{10M3h} hydrogenation catalyst isosorbide was synthesized from cellulosic substrates and glucose under the optimized two-step reaction conditions, to see how the results compare with the corresponding reactions conducted with the commercial Ru/C (Table 3). Astonishingly, in addition to the good recyclability with BP, the best RuO_x/C_{10M3h} catalyst generated isosorbide from the cellulosic substrates in higher yields than the commercial hydrogenation catalyst.

Table 3 The isosorbide yields under the optimal two-step reaction conditions using RuO_x/C_{10M3h} as the hydrogenation catalyst.

Substrate	Time (h)	Temperature (°C)	Isosorbide yield (%) ^b
BP	2 + 6	170 + 200	57
MCC	2 + 6	170 + 200	56
DP	2 + 6	170 + 200	56
Glucose	2 + 6	170 + 200	65

^a Reaction conditions: the first step reaction conditions: 170 °C, 20 bar H₂, 2 h and 0.02 mmol of second run RuO_x/C_{10M3h}. Between the reaction steps the RuO_x/C_{10M3h} was collected *via* filtration and the second step was conducted with the filtrate. The second step reaction conditions: 200 °C, 40 bar H₂, 6 h; ^b The yields were obtained with HPLC-RID using calibration curves.

We also investigated the deactivation of the hydrogenation catalyst in the two-step reaction setup. The deactivation through leaching, sulfur poisoning or mechanical alterations (attrition and crushing) were ruled out, as the deactivation was substrate dependent. However, these mechanisms might cause problems in longer use. We conducted transmission electron microscope (TEM) measurements on fresh and used hydrogenation catalysts. The measurements revealed that the particle size grows during the runs and the particle growth is very different between the commercial and synthesized catalysts. The particle size of the commercial Ru/C grew from 2.66 nm to 2.98 nm during five consecutive runs with MCC, whereas the average particle size of the modified RuO_x/C_{10M30min} went from 2.48 nm to 4.84 nm in four runs with BP as the substrate under the optimized first step reaction conditions (Figure 28). This growth of the particle size indicates that the deactivation was not caused by sintering, as both catalysts retained their activity at good levels during the experiments. However, X-ray powder diffraction (XRD) measurements revealed a build-up of unknown substance on the four times used RuO_x/C_{10M30min} with BP as substrate, indicating that the deactivation was caused by fouling or poisoning, most likely by lignin.

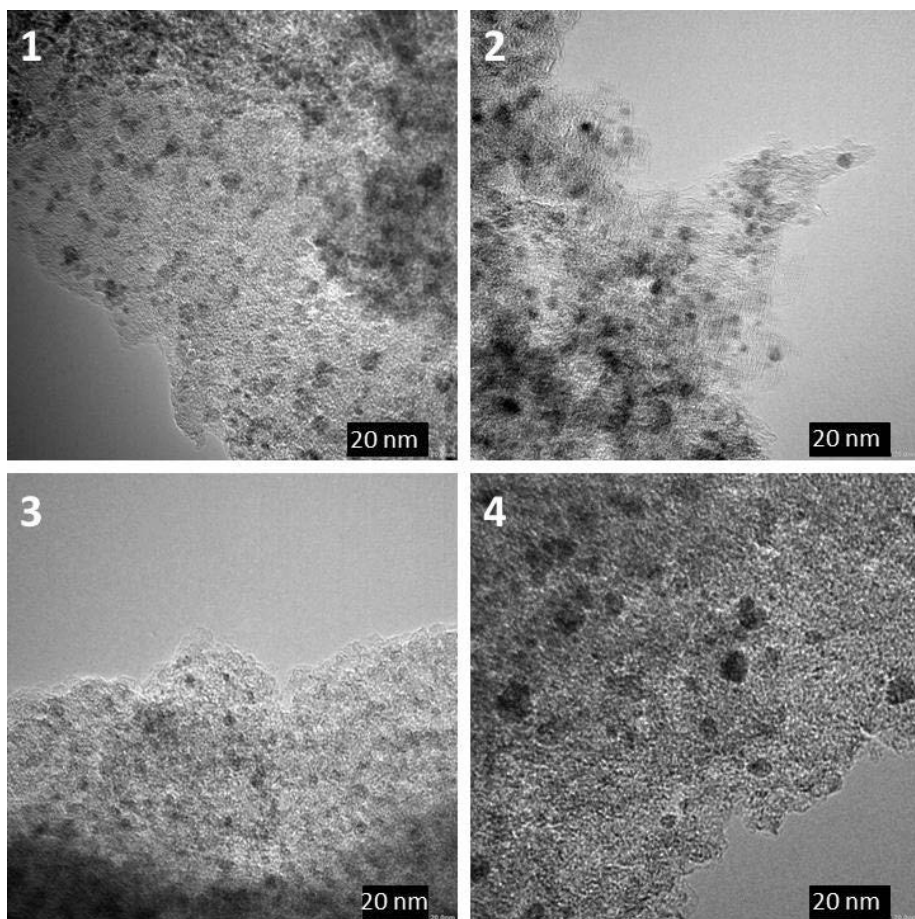


Figure 28 TEM images of 1) fresh commercial Ru/C, 2) five times used commercial Ru/C, 3) fresh RuO_x/C₁₀M₃₀min, and 4) four times used RuO_x/C₁₀M₃₀min.

In this work, the synthesis of isosorbide from different cellulosic substrates in aqueous solution was studied. In the reaction optimization, Ru/C and H₂SO₄ were found to be the best catalysts; and the two-step step system proved to increase the recyclability of the commercial Ru/C with pure cellulosic substrates, MCC and DP. However, with the lignin-containing BP the recyclability of the commercial Ru/C was drastically decreased, resulting in the formation of FA and LA after the second run. Accordingly, the hydrogenation catalysts were modified by increasing the acidity, and thus hydrophilicity, of the support material to improve the recyclability with BP as substrate. The acidifying treatments, H₂SO₄ treatment and oxidation, on the catalyst proved to enhance the recyclability significantly with BP as substrate. This was thought to arise from the diminished interactions of the fouling and poisoning agents with the catalyst. With the use of the best hydrogenation catalyst RuO_x/C₁₀M_{3h} we were able to obtain 56-57 mol.% (49-50 wt.%)

isosorbide yields from cellulosic materials and the catalyst could be recycled at least four times with lignin containing substrate without losing its activity. Our studies indicate that fouling and poisoning, presumably by lignin, were the main deactivation mechanisms in short-term use under these conditions.

4.3 CONVERSION OF ALCOHOLS, ETHERS, AND ESTERS TO OLEFINS (PUBLICATION III)

Nature produces plenty of different organic compounds with oxygen containing functionalities, such as alcohols, esters, and ethers. Through removal of oxygen species from these compounds, biopolymer applicable alkenes can be synthesized. One of the naturally abundant class of compounds are monoterpene alcohols, which can be converted into various olefins *via* dehydration.^[5] At the moment, the olefins for polymer applications are mainly produced from petroleum-based feedstocks. In this work, we studied transition metal triflate-catalyzed dehydration of alcohols and monoterpene alcohols as well as the conversion of octyl acetate and dioctyl ether to olefins.

The work began by studying the effect of the oxophilicity and Lewis acidity of the metals in the dehydration of 2-octanol to octenes, using mainly triflate salts as the catalysts (Figure 29). The reactions were conducted in closed reaction vessels, which were heated at 150 °C in an oil bath for 3 hours under solvent-free conditions using a catalyst loading of 0.5 mol.%. The oxophilicity was addressed in terms of the dissociation energy of the M-O bond and the Lewis acidity was calculated using the following equation, Lewis acidity = Z/r^3 (1/pm³), where Z = charge of the metal cation and r = ionic radii of the metal cation.^[181–183] The effect of the triflate anions on the Lewis acidity was neglected in the calculations.

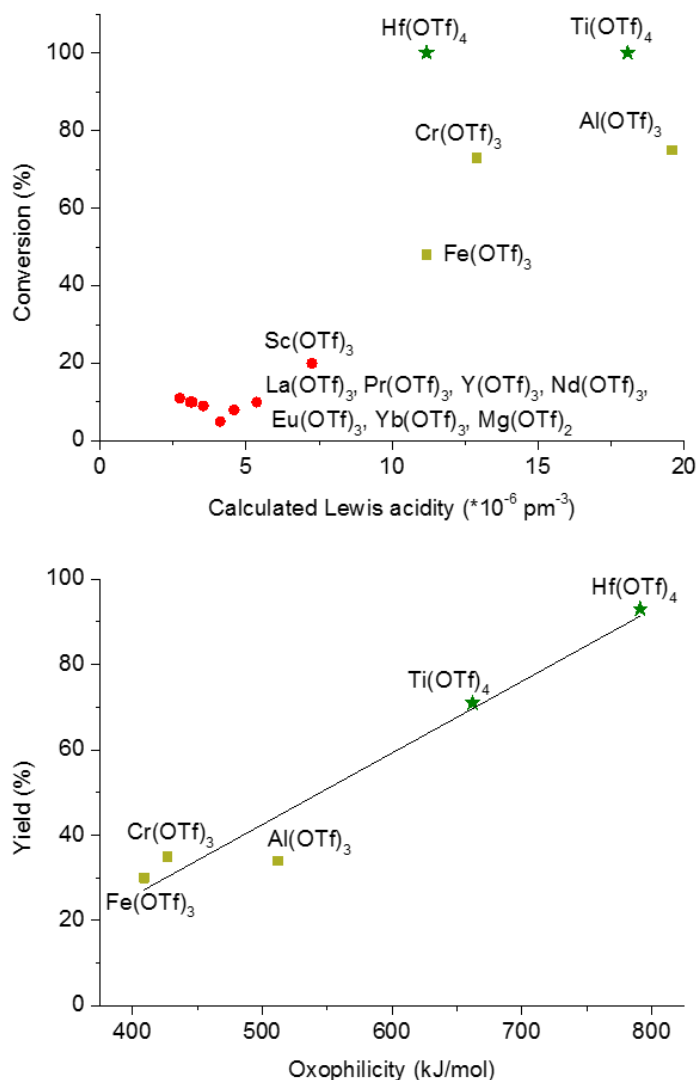


Figure 29 The effect of Lewis acidity (top) and oxophilicity (bottom) of the metal on the metal triflate-catalyzed dehydration of 2-octanol.

The metal triflates that generated satisfactory conversions, Fe(OTf)₃, Cr(OTf)₃, Al(OTf)₃, Ti(OTf)₄, and Hf(OTf)₄, had calculated Lewis acidities over $1 \times 10^{-5} \text{ pm}^{-3}$. The larger and lower oxidation state metal triflates facilitated low conversion of 2-octanol. The correlation of the yield of octenes and the oxophilicity of the metals seemed to be linear with the sufficiently Lewis acidic metal catalysts. The higher oxophilicity facilitated higher octene yields: with the most oxophilic Hf(OTf)₄ the octene yield was 93% and the least oxophilic Fe(OTf)₃ generated only a 30% yield. The yields obtained with the rest of the metal triflates fitted appropriately in between Fe(OTf)₃ and Hf(OTf)₄ in a linear fashion in respect of the oxophilicities. Furthermore, the dehydration of

2-octanol conducted at elevated temperature, 165 °C, using $\text{Fe}(\text{OTf})_3$, $\text{Cr}(\text{OTf})_3$, and $\text{Al}(\text{OTf})_3$ as catalysts boosted the octene yields to 80%, 84%, and 85%, respectively, along with quantitative conversions. Next, we moved on to study the conversion rates with the five best catalysts, by monitoring the conversion of 2-octanol at 150 °C with respect to time (Figure 30).

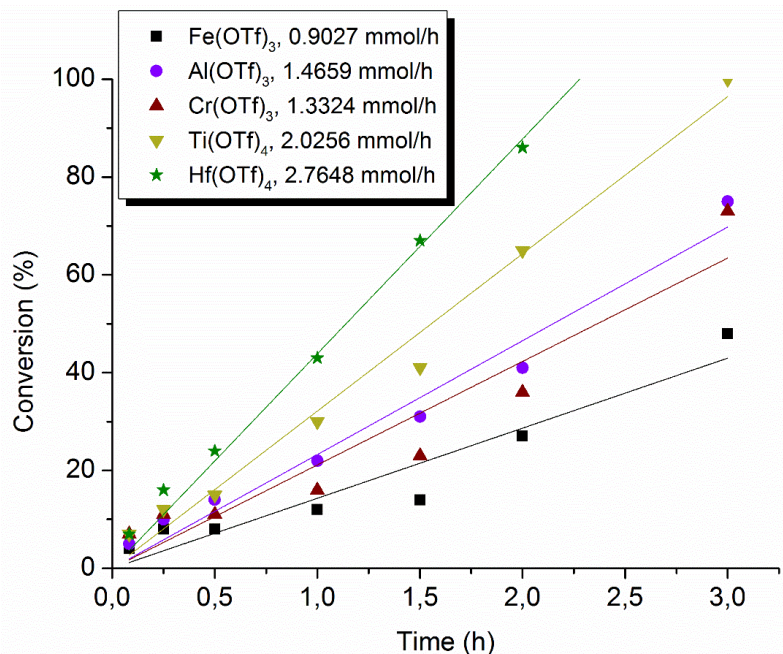
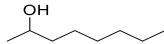
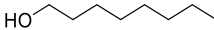

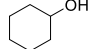
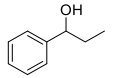
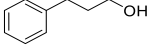
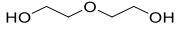
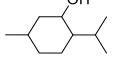
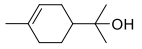
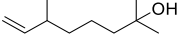
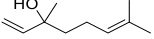
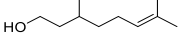
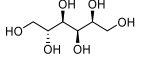

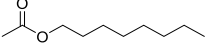


Figure 30 The conversion of 2-octanol in the respect to time and the calculated conversion rates of the best transition metal triflates.

The conversion rates were found to decrease in the order $\text{Hf}(\text{OTf})_4 > \text{Ti}(\text{OTf})_4 > \text{Al}(\text{OTf})_3 > \text{Cr}(\text{OTf})_3 > \text{Fe}(\text{OTf})_3$, similarly to the octene yields obtained in the initial studies. Moreover, the linear conversion of 2-octanol with respect to time indicated that the reaction kinetics is zero-order. The zero-order reaction is typical in this kind of reaction setup, where the substrate-to-catalyst ratio is high. In this environment, the catalysts were saturated and thus they worked at their maximum conversion rate, facilitating comparable results. We continued our studies with $\text{Fe}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$, by examining the dehydration of additional model alcohols, monoterpene alcohols as well as dioctyl ether and octylacetate (Table 4). As a result of the more encouraging 2-octanol dehydration outcome at 165 °C with $\text{Fe}(\text{OTf})_3$, most of the $\text{Fe}(\text{OTf})_3$ -catalyzed dehydrations were conducted at higher temperatures than with $\text{Hf}(\text{OTf})_4$. Based on the initial studies and rate of conversion, the reaction outcomes with $\text{Al}(\text{OTf})_3$, $\text{Cr}(\text{OTf})_3$, and $\text{Ti}(\text{OTf})_4$ could be expected to be in between $\text{Fe}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$.

Table 4 The highest olefin yields with different substrates using Fe(OTf)₃ and Hf(OTf)₄ as the dehydration catalysts.

Entry	Substrate	Hf(OTf) ₄			Fe(OTf) ₃		
		Yield (%) ^a	t (h)	T (°C)	Yield (%) ^a	t (h)	T (°C)
1		85	1.5	150	91	3	165
2		65	12	180	2	6	180
3		84	0.5	110	79	0.5	130
4		78	3.5	150	80	2.5	165
5		3	0.5	110	3	0.5	130
6		N.d.	6	180	-	-	-
7		85 ^b	4.5	180	-	-	-
8		82	3	150	71	4	165
9		16	0.5	110	76	0.5	130
10		84	0.5	110	82	0.5	130
11		3	0.5	110	3	0.5	130
12		7	24	180	-	-	-
13		78 ^c	3	130	77 ^c	3	150
14		29 ^d	24	180	N.d. ^d	24	180
15		80	24	180	68	36	180

Reaction conditions: Catalyst loading 0.5 mol.% of the substrate and reactions were conducted in a flask connected to micro distillation apparatus; ^a Isolated olefin yields, products analyzed with ¹H NMR, ¹³C NMR and gas chromatograph equipped with mass spectrometer detector (GC-MS); ^b 1,4-dioxane as the product; ^c Batch type reactions were conducted *in vacuo*, isosorbide yields were obtained with HPLC-RID and calibration curves; ^d Reactions were conducted in a closed reaction vessel (batch type) in the presence of water (1 eq.) and the yields were obtained with GC-FID using calibration curves. N.d. = not detected.

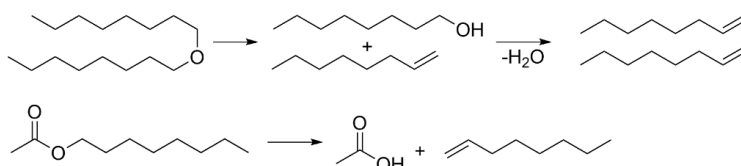
The substrate studies were conducted in a flask connected to a micro distillation apparatus, which enabled isolation of the reaction products, olefins and water through distillation as they formed. Some experiments were conducted under reduced pressure to allow the distillation. The distilled products, olefins and water, were then placed into a freezer to allow the separation of the liquid olefins from the frozen water simply by pipetting. The dehydration of 1-octanol, 2-octanol, and 3-ethylpentan-3-ol using $\text{Hf}(\text{OTf})_4$ generated alkenes in 65%, 85%, and 84% isolated yields, respectively (Table 4, Entries 1-3). The corresponding alkene yields with $\text{Fe}(\text{OTf})_3$ were 2%, 91%, and 79%, where 1-octanol formed mainly dioctyl ether as the product. The comparison of the reaction outcomes and conditions of the alcohol dehydration experiments allowed us to conclude that the conversion of tertiary alcohols is the most facile, followed by the secondary alcohols, primary alcohols being the most challenging. As a result of the poor 2% yield of olefins from 1-octanol, no further $\text{Fe}(\text{OTf})_3$ -catalyzed primary alcohol dehydration experiments were conducted. Furthermore, cyclohexanol was converted to cyclohexene in good 78-80% yields with both of the metal triflates used (Entry 4), whilst the use of aromatic alcohols as substrates generated poor dehydration product yields, and formation of a viscous oily substance was observed even at lower temperatures, presumed to arise from oligomerization (Entries 5 and 6). The dehydration of diethylene glycol generated 1,4-dioxane in good 85% isolated yield in 4.5 hours with the $\text{Hf}(\text{OTf})_4$ catalyst (Entry 7).

Due to the challenging dehydration of the primary alcohols, the study of terpene alcohol dehydration focused on secondary and tertiary alcohols. As with the other alcohols, the dehydration is more efficient with $\text{Hf}(\text{OTf})_4$ than with $\text{Fe}(\text{OTf})_3$. The $\text{Fe}(\text{OTf})_3$ - and $\text{Hf}(\text{OTf})_4$ -catalyzed dehydration of menthol and dihydromyrcenol generated olefins in good yields of 71-84% (Entries 8 and 10). However, the conversions of linalool, citronellol, and α -terpineol to olefins proved to be more challenging (Entries 9, 11, and 12). Like the aromatic alcohols, with the use of $\text{Hf}(\text{OTf})_4$ as the catalyst, all of these substrates formed non-volatile oily substances and generated rather low 3-16% yields of distillable octenes. The use of $\text{Fe}(\text{OTf})_3$ in place of $\text{Hf}(\text{OTf})_4$ in the dehydration of α -terpineol enhanced the olefin yield from 16% to 76%. Unfortunately, this could not be replicated with linalool, since a similar 3% olefin yield was obtained. All of the secondary and tertiary alcohols that generated poor olefin yields have an electron-donating group, such as methyl group connected to double-bonded carbon atom. These kind of structures are known to facilitate cationic polymerization in the presence of metal halide salts, thus it is probable that the non-volatile oils are oligomers forming through cationic polymerization.^[44,184] It seems that the stronger dehydration catalyst $\text{Hf}(\text{OTf})_4$ sets off the proposed cationic polymerization more easily than $\text{Fe}(\text{OTf})_3$, as exemplified in the α -terpineol dehydration. The dehydration of sugar alcohols was studied using sorbitol as the substrate, as it is readily available from cellulose.^[185] The $\text{Fe}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$ -catalyzed dehydration of sorbitol generated isosorbide in 77% and 78% yields, respectively. The obtained

isosorbide yields are comparable to previously published metal triflate-catalyzed sorbitol dehydration, although the use of $\text{Fe}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$ generated isosorbide in shorter reaction time and with lower catalyst loading.^[186] In general, similar olefin yields were obtained with both the metal triflates, although the use of $\text{Hf}(\text{OTf})_4$ enabled the efficient dehydration of alcohols at lower temperatures than $\text{Fe}(\text{OTf})_3$. Additionally, it should be noted that ^1H and ^{13}C NMR studies revealed formation of olefin isomer mixtures with all of the substrates except for cyclohexanol, 3-ethylpentan-3-ol, and diethylene glycol (Entries 3, 4, and 7). The formation of the isomers were thought to arise from the migration of the charge during carbocation transition state.

The study was continued by investigating the conversions of dioctyl ether and octyl acetate to octenes (Table 4, Entries 14 and 15). Two different approaches were devised for this conversion, direct C-O bond cleavage and hydrolysis of the ether and ester bonds (Figure 31). The direct cleavage of dioctyl ether was envisaged to proceed through the initial C-O ether bond cleavage forming octenes and 1-octanol, followed by the dehydration of 1-octanol to another octene molecule. The hydrolysis of dioctyl ether, on the other hand, would proceed through the formation of two 1-octanol molecules and their subsequent dehydration to octenes. According to the literature, esters can be hydrolyzed at the acyl and alkoxy positions, of which the alkoxy C-O cleavage is more common.^[172] Thus, we assumed that the hydrolysis and the direct cleavage of the octyl acetate ester group would proceed *via* the alkoxy C-O scission, forming AcOH, 1-octanol and octenes, followed by their possible dehydration to alkenes.

Direct C-O cleavage



C-O cleavage through hydrolysis

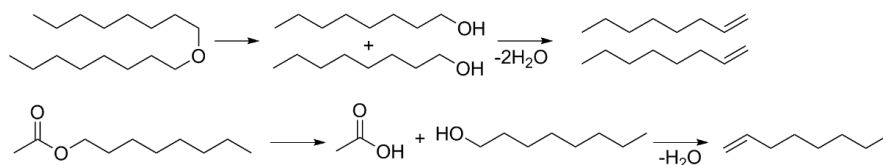


Figure 31 The pathways of the olefins synthesis from dioctyl ether and octyl acetate.

The conversion of dioctyl ether to octenes was only successful using the hydrolysis pathway in the presence of $\text{Hf}(\text{OTf})_4$ (Table 4, Entry 13). However, even under the best conditions only a modest 29% yield of octenes was

obtained due to incomplete hydrolysis of the ether bond and the cumbersome dehydration of 1-octanol. With the use of $\text{Fe}(\text{OTf})_3$, no octene formation from dioctyl ether was achieved. Amazingly, the direct cleavage of octyl acetate occurred as assumed, through the alkoxy C-O bond cleavage, and as a result, AcOH and octenes were isolated as the reaction products. Furthermore, the direct C-O cleavage approach resulted in good octane yields from octyl acetate, as 68% and 80% isolated yields were achieved with $\text{Fe}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$, respectively. The use of the hydrolysis pathway with octyl acetate resulted in the formation of 1-octanol, which thus hampered the formation of the octenes. According to these results, we may conclude that the metal triflate-catalyzed removal of oxygen containing functionalities occurs in the order of *tert*-alcohols>*sec*-alcohols>esters>*prim*-alcohols>ethers. No conversion of carboxylic acids was achieved with the metal triflates, and aldehydes reacted almost instantly, forming non-volatile oily substances assumed to be oligomers.

The study was concluded by conducting dehydration of 2-octanol to octenes on a larger scale and the conversion of tea tree oil to olefins as proof-of-concept studies. The large-scale conversion was conducted with 144.9 mmol of 2-octanol and with 0.06 mmol of catalyst, where the substrate was added dropwise to the heated flask with the use of a dropping funnel, with the products being distilled off using a micro distillation apparatus. This generated octenes in 84% and 80% yields with $\text{Hf}(\text{OTf})_4$ in 10 hours and $\text{Fe}(\text{OTf})_3$ in 24 hours, respectively. The conversion of tea tree oil to olefins was only achieved with $\text{Fe}(\text{OTf})_3$ due to the large amount of terpinen-4-ol, which formed oligomers in the presence of the stronger $\text{Hf}(\text{OTf})_4$ catalyst. We were able to obtain 53 wt.% of olefins from the tea tree oil in one hour using $\text{Fe}(\text{OTf})_3$ as the catalyst at 130 °C under a reduced pressure of 57 mmHg.

In this work, the conversion of oxygen-containing functionalities to olefins using abundant transition metal catalysts was studied under solvent-free conditions. We found that metal atoms need to be highly Lewis acidic and oxophilic in order to work as efficient dehydration catalysts. The triflate anion increased the catalytic activity due to its Lewis acidity enhancing ability to withdraw electrons from the central metal. These findings could serve as guidelines for the future development of the defunctionalization catalyst. The conversion of model and monoterpene alcohols revealed that tertiary alcohols are the most easy to remove, followed by secondary alcohols and primary alcohols, which are the most challenging. This ranking followed the stability order of the carbocations. Mainly, good olefin yields were obtained from secondary and tertiary alcohols using $\text{Hf}(\text{OTf})_4$ and $\text{Fe}(\text{OTf})_3$ as catalysts. Only $\text{Hf}(\text{OTf})_4$ generated octenes from 1-octanol in respectable yields. Substrates containing electron-donating groups, such as a methyl group, next to the C=C double bonds were found to form non-volatile oils as products. The electron-donating groups are known to facilitate cationic polymerization, and this was thought to be the formation mechanism of the oily products. Furthermore, the conversion of dioctyl ether to olefins was only possible through hydrolysis of

the ether C-O bond, forming 1-octanol as products, and thus, the octene yields were low, 29% at best. The conversion of octyl acetate to AcOH and octenes was achieved in direct alkoxy C-O cleavage fashion in the absence of water with both of the studied catalysts, generating octenes in 68-80% yields. The proof-of-concept experiments showed that the catalysts are very robust and efficient with the capability to generate olefins from biomass-based essential oils.

5 CONCLUSIONS

The catalytic defunctionalization of high oxygen content biomass can provide alternative starting materials to replace petroleum-based feedstocks in various applications. As a result, the modification of biomass-based products has been under intensive investigation. The current setups mostly generate good product yields on the laboratory scale, but as a drawback, their applicability on larger scales is not yet feasible. Because of this, the need for further catalyst development and more efficient reaction setups is acute. The prospect of increasing the lifetime of the catalysts and the use of abundant elements as catalysts should be a high priority in the future studies.

The thesis was aimed to contribute to the research of more efficient and sustainable catalytic conversion of biomass-based substrates to value-added chemicals. In this respect, new one-step $\text{Eu}(\text{OTf})_3$ and Pd/C -catalyzed HDO setup for conversion of furfurals to alkanes was developed. This highly selective method provides diesel-range C_{11} and C_{12} alkanes from furfural and HMF derivatives in high yields. The one-step system decreases the required time to generate the alkanes from the substrate furfural derivatives. Furthermore, the study also demonstrated the effect of the solvent and the substrates of the furan ring on the reaction outcome.

The author also studied the catalytic conversion of cellulose to isosorbide. Generally, the hydrogenation catalysts undergo rapid deactivation, most often by poisoning and fouling, even with lignin-free substrates. We set out to develop a new recyclable hydrogenation catalyst that tolerates the presence of lignin. The optimized two-step reaction conditions and the acidifying treatments on the ruthenium catalyst enabled the efficient recycling of the catalyst with lignin containing cellulose, also generating high yields of isosorbide.

The defunctionalization of oxygen containing substrates were studied with metal triflates. During this study, we demonstrated the effect of oxophilicity and Lewis acidity of the metals on the dehydration of 2-octanol using different metal triflate salts. With the most efficient catalyst, $\text{Hf}(\text{OTf})_4$, as well as abundant and inexpensive $\text{Fe}(\text{OTf})_3$, the conversion of various alcohols, terpenoids, dioctyl ether, and octyl acetate to olefins was studied. The investigation revealed that most secondary and tertiary alcohols and octyl acetate could be converted to olefins in high yields using the transition metal triflates. Furthermore, the robustness of the catalysts and their ability to convert tea tree oil to olefins was demonstrated successfully.

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